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Photochemical Initiation of Detonation in Gaseous Explosive Media

By

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During this investigation a study was made of photochemical initiation of
detonation in gaseous explosive media. The study is judged relevant to the
development of the single event third generation FAE weapons. The flash photo-
lysis technique was used to investigate the mechanisms of photochemical initiation
of detonative chemical reactions in sub-atmospheric explosive gaseous mixtures
of H_2-Cl_2 and C_2H_2-O_2 with and without NO_2 sensitization. Results conclusively
demonstrate the feasibility of initiation of detonation by the free radical mode
of initiation. Direct initiation of detonation is produced after some critical

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induction time provided the initial free radical concentration exceeds the limiting critical value characteristic of the particular explosive medium. Three regimes of late time propagation can be generated by varying the flash intensity. With increasing flash energy the deflagrative, transitional and detonative regimes, reminiscent of those initiated by the thermal blast mode, have been produced using photochemical initiation. The mechanisms of initiation, however, are drastically different for the two modes. In photochemical initiation, the development of combustion waves is due to the exothermicity of chemical reactions consequent to the injection of the free radicals. In the thermal modes, initiation occurs thermally via auto-ignition of reaction in the wake of a decaying blast. The results show that for photochemical initiation, deflagrative, transitional or detonative combustion waves develop from a diffuse region of chemical reactions corresponding to the highest initial concentration of free radicals. The development of the combustion waves occurs subsequent to the rapid evolution of a shock wave from this region of diffuse chemical activity. With more intense radiation than that necessary for direct initiation of detonation, the strength of the detonation front decreases with increasing flash energy. This is attributed to chemical pre-activation via dissociation of the explosive gas medium ahead of the advancing detonation front. It is expected that with very intense irradiation, volumetric initiation of chemical reactions throughout the entire gas medium could be achieved. To the best of our knowledge, the results of the present study are the first ever to elucidate in detail the mechanisms of photochemical initiation of detonation in gaseous explosive media.

ABSTRACT

The present paper reports the results of a study of photochemical initiation of detonation in gaseous explosive media. The study is judged relevant to the development of the single event third generation FAE weapons. The flash photolysis technique was used to investigate the mechanisms of photochemical initiation of detonative chemical reactions in sub-atmospheric explosive gaseous mixtures of H_2-Cl_2 and $C_2H_2-O_2$ with and without NO_2 sensitization. The results conclusively demonstrate the feasibility of initiation of detonation by the free radical mode of initiation. Direct initiation of detonation is produced after some critical induction time provided the initial free radical concentration exceeds the limiting critical value characteristic of the particular explosive medium. Three regimes of late time propagation can be generated by varying the flash intensity. With increasing flash energy the deflagrative, transitional and detonative regimes, reminiscent of those initiated by the thermal blast mode, have been produced using photochemical initiation. The mechanisms of initiation, however, are drastically different for the two modes. In photochemical initiation, the development of combustion waves is due to the exothermicity of chemical reactions consequent to the injection of the free radicals. In the thermal modes, initiation occurs thermally via auto-ignition of reaction in the wake of a decaying blast. The results show that for photochemical initiation, deflagrative, transitional or detonative combustion waves develop from a diffuse region of chemical reactions corresponding to the highest initial concentration of free radicals. The development of the combustion waves occurs subsequent to the rapid evolution of a shock wave from this region of diffuse chemical activity. With more intense radiation than that necessary for direct initiation of detonation, the strength of the detonation front decreases with increasing flash energy. This is attributed to chemical pre-activation via dissociation of the explosive gas medium ahead of the advancing detonation

front.   It is expected that with very intense irradiation, volumetric initia-
tion of chemical reactions throughout the entire gas medium could be achieved.
To the best of our knowledge, the results of the present study are the first
ever to elucidate in detail the mechanisms of photochemical initiation of
detonation in gaseous explosive media.

1. Introduction

The present report describes the results of a study of a novel mode of detonation initiation in a gaseous explosive medium. The essence of this technique is that initiation is achieved by chemical, rather than thermal means. In this chemical mode of initiation, the primary initiating step in the development of explosive reactions is via the rapid production of free radicals in the gaseous medium itself. The main secondary explosive reaction in the fuel-air mixture then proceeds spontaneously and automatically after an induction time and without further external intervention provided the free radical concentration produced in the primary reaction exceeds a certain critical threshold level. The free radical production can be triggered by auto-dissociation via a catalyst injected and dispersed in the detonating gas or by stimulated dissociation of one of the constituents (or of a sensitizer) by external means, eg., flash photolysis. In the present study, the photo-dissociation or the flash photolysis technique has been used exclusively as the free radical producing process. The basis for the choice was one of convenience since the technique readily lends itself to quantitative variation of the concentration of free radicals produced, as well as of the rate of their production. This flexibility was particularly important in the present study since emphasis was placed on elucidating the detailed mechanisms of this mode of initiation which implied as wide a variation of parameters as possible, while preserving the essential universal features of the phenomenon.

The mechanisms underlying the free radical mode of detonation initiation are drastically different from those for the thermal modes of initiation in which detonation is produced from accelerating flames [1-3] or from blast waves in a detonating gas [4-7]. These two latter modes of initiation have been extensively studied over the span of the past two

decades and the understanding of the underlying mechanisms has reached a functionally satisfactory degree of completeness. In particular, the blast initiation technique has been exploited successfully in the development of the second generation of FAE weapons. Currently, however, the free radical mode of detonation initiation appears to have great potential interest in the context of the single event third generation of FAE weapons. In such devices the radical producing chemical catalyst would be disseminated simultaneously with the fuel in the formation of the explosive vapor cloud. Explosive reactions would then proceed automatically throughout the vapor cloud after a characteristic delay as a result of the chemical action of the free radicals in initiating such reactions. The most effective version of such a weapon would be one for which the induction time for the development of chemical reactions via the free radicals would be adjusted to correspond to the time scale for the mixing of the fuel with the ambient air to explosive proportions over most of the span of the vapor cloud. It is evident, therefore, that the successful development of an effective third generation FAE weapon is contingent upon the ability to control a number of time scales inherent in the coupled chemico-kinetic and gasdynamic processes underlying this mode of initiation. As of the present time, relatively little is known about the detailed mechanisms of initiation of detonation via chemical sensitizers. Hence, the ability to control events to the extent that would be necessary in a functional third generation FAE weapon is at present completely lacking and must await the resolution of a number of fundamental problems in this area. Although in the past thirty years there has been some work done in the area of free radical initiation and enhancement of chemical reactions using flash photolysis, no direct concentrated efforts were made to study detonative combustion via such initiation per se. For example, in the classical work of Norrish, Porter and Thrush[8-11] in the early fifties on photochemistry, there is indirect evidence that detonation

was produced[11]. However, their attitude at the time was that such occurrences produced spatial and temporal inhomogeneities which was an undesirable experimental complication to be avoided in the context of the main thrust of their work in photochemistry for which a homogeneous medium was required. The other main research done in this area is the more recent work of Cerkanowicz et al[12-14] who investigated the initiation of chemical reactions by flash photolysis in non-sensitzed media of methane-oxidizer and hydrogen-oxidizer gaseous mixtures. Their work was concerned with enhancing combustion in supersonic propulsion systems and did not include a study of detonative combustion. Perhaps the only reported situation where detonative combustion was produced intentionally and directly by flash photolysis was by Wadsworth[15] who restricted himself to using the technique to generate imploding waves.

The main thrust of the present work, therefore, has been to address itself directly to the problem of detonation initiation by chemical sensitizers in order to build up the necessary fundamental understanding of the mechanisms involved so that this in turn could be applied to the development of the third generation FAE devices. The approach has been first to identify the problem areas and then to investigate them systematically each in turn. The overall problem is broken down into a number of specific tasks which are outlined below and are discussed sequentially in detail in the remainder of the report. The tasks are:

i) to confirm the feasibility for direct initiation of detonation via the free radical mode of initiation,

ii) to explore the quantitative link between the free radical concentration and the induction time for chemical reactions in some typical explosive medium,

iii) to identify the detailed wave processes occuring during initiation,

iv)   to elucidate the detailed mechanisms of this mode of initiation, i.e.,
to establish the detailed sequence of events between the time of
injection of the free radicals and the time of evolution of the detona-
tion.

2. Direct Initiation of Detonation

To confirm the feasibility of direct initiation of detonation by
the free radical mode of initiation, a series of experiments were performed
which for reasons of speed and convenience employed an existing solid state
laser system that could be readily modified for the flash photolysis experi-
ments. The schematic diagram in Fig. 1 illustrates the essential part of
the apparatus. The modification involved the replacement of the central neo-
dymium laser rod in the double elliptical silvered laser cavity by a UV
transmitting quartz cell which could be filled with the explosive gas sample.
Figs. 2 and 3 display actual photographs of the laser cavity modified in
this way. The quartz explosion tube was 14 mm ID, 1 mm wall thickness and
about 40 cm long and was inserted inside the laser cavity which is 16 cm long.
The cavity was irradiated by two xenon flash lamps (EG & G FX47C) and was
flushed with dry nitrogen to protect the silvered surfaces. The flash lamps
and the explosion tube inside the cavity were cooled by a continuous flow of
water at about $0^{\circ}C$. The explosion tube was instrumented with calibrated
piezoelectric transducers (PCB 113A24) inserted at the two ends of the tube.
In some of the experiments, one of the transducers was removed and a 120 cm
long glass tube extension of the quartz cell was added to protrude beyond
the ignition cavity. A detailed schematic diagram of the entire experimental
system is illustrated in Fig. 4. A streak camera was used to observe the
combustion processes in the length of tube extending beyond the cavity. The
two flash lamps were pumped by an energy bank consisting of 2250 μf at 4KV
maximum. A phototube (RCA 929) monitored the light output of the flash tube

so that various events could be referenced to the start of the light emission inside the cavity. Explosive mixtures of $C_2H_2-O_2$, H_2-O_2 and H_2-Cl_2 were prepared in steel storage tanks and allowed to mix by diffusion for at least 24 hours before use. The range of initial pressures in the present experiments was from 10 to 150 torr. The 1 mm wall thickness of the present quartz explosion tube could not withstand the detonation pressures exceeding that corresponding to mixtures with $p_o \approx 150$ torr. To cause easier ignition, the explosion mixtures of $C_2H_2-O_2$ were sensitized with NO_2 in some experiments. Nitrogen dioxide absorbs light readily in the range of wavelengths from 3000 Å to 5000 Å (Fig. 5); H_2-Cl_2 mixtures need not be sensitized because Cl_2 absorbs readily in the range 2500 Å to 4000 Å. If no NO_2 is used for sensitization, then atomic oxygen production depends solely on the photodissociation of O_2. Oxygen absorbs from the Schumann Runge band of 1350 to 1700 Å down towards the far UV. The quartz tube used in the present experiments cuts off sharply at about 1650 Å. Thus very little of the light is useful in initiating the reactions if no sensitizers are used. If a sapphire or lithium fluoride tube were used throughout and air spaces between the flash and the explosion tube eliminated (since air absorbs UV) then sufficient light in the far UV would be available for photo-dissociation of O_2 and explosion could be initiated readily without the use of NO_2 or other sensitizers. There was no need to avoid the use of sensitizers in the present sutdy of detonation initiation.

The results of the present experiments conclusively demonstrate direct initiation of detonation in all the mixtures ($C_2H_2-O_2$, H_2-O_2, H_2-Cl_2) tested in the pressure range of 10 to 150 torr could be achieved. The flash duration is about 2 milliseconds and if the start of the flash is taken as the reference time $t = 0$, then after a delay typically of the order of a few hundred microseconds, a sudden pressure rise in the cavity is observed as registered by the pressure transducer at the ignition end of the explo-

sion tube. The pressure rise is sharp and its magnitude corresponds to about the reflected C-J (in fact slightly overdriven) detonation pressure for the particular mixture. This demonstrates the formation of a detonation inside the volume of the explosion tube excited by the flash. A typical pressure and light output of the flash (superimposed on one trace) are shown in Fig. 6. In this case the explosion is formed before the light output attains its peak value. Simultaneous recording by the streak camera looking at the remaining 120 cm of the explosion tube outside the ignition cavity shows that after the delay time of about the same as that from the pressure record, a fully developed C-J detonation wave emerges from the ignition cavity (Fig. 7). No pre-detonation flame is observed (except at very low pressures or in fuel-air mixtures) indicating that the detonations is formed instantaneously in the volume excited by the flash. Depending on the amount of sensitizers used (i.e., NO_2 concentration), the energy of the flash, the initial pressure and composition of the mixture, and the chemical system itself, the induction delay time (i.e., from the beginning of the flash to the appearance of the detonation) is different (Fig. 8). The results show the general behavior, namely that the induction delay decreases with 1) increasing sensitizer (i.e., NO_2) concentration, ii) increasing initial pressure p_o and iii) increasing flash energy. This result is to be expected. The pressure dependence (in the range of 20 to 100 torr) is not very strong. The H_2-Cl_2 system has the minimum induction times while the H_2-O_2 system has the maximum. With NO_2 as sensitizer, C_2H_2-air mixtures can also be detonated. With sufficiently high flash energy detonation can be initiated in C_2H_2-O_2 even without the use of NO_2 as sensitizers. Typically, the induction times for all the experiments performed are below 1 millisecond (Fig. 8).

There were some doubts initially, concerning whether or not the detonation is formed instantaneously inside the excited volume. What could

happen is that the excited volume first burns with a pressure rise correspond-
ing to that for constant volume combustion. Then the subsequent expansion of
the combustion product gases into the unburned mixture outside the cavity
will drive a shock into the unburned mixtures outside the cavity. If the
shock wave is sufficiently strong then it can form a detonation wave. Thus
a shock tube calculation was performed to verify this. Assuming the pres-
sure rise inside the cavity corresponds to that for constant volume com-
bustion, the calculations indicated that the strength of the shock trans-
mitted to the unburned gases is about $M_s = 2$, too weak to even cause auto-
ignition in the unburned mixture outside the cavity (Fig. 9). This con-
clusively shows that detonation must have been formed within the excited
portion of the explosion tube inside the cavity itself.

A series of experiments were next performed to obtain a more
detailed pressure history of the explosion processes inside the excited
volume. Two calibrated quartz PCB pressure transducers were used (one at
either end) to record the explosion pressure in various lengths of the
explosion tube ranging from 4 cm to 36 cm long. Using the 36 cm tube, the
excited volume is the central 16 cm of the tube and 10 cm of unexcited
lengths stick out from either end of the flash cavity. The tube ends are
closed by the two calibrated PCB quartz transducers. In Fig 10a, we note that
after a delay of about 460 µsec, the two PCB's record a sudden pressure
rise which quantitatively corresponds to a pressure slightly above the re-
flected pressure of a Chapman-Jouguet wave in the mixture. Thus a slightly
overdriven detonation wave is formed in this case. This experiment proves
that detonative combustion must have occured inside the cavity itself be-
cause the usual predetonation distance for this mixture is of the order of
a meter if a flame were to be initiated inside the excited volume and
transition to take place outside in the remaining 10 cm length. The pressure

traces also demonstrate that a series of pressure waves are bouncing back and forth inside the explosion tube. These waves originate from the reflection of the detonations from the ends of the tube. In Fig. 10b aluminum foil is used to mask off everything but the central one third of the explosion tube. Thus only the central part of the tube in the cavity corresponding to about 5 cm length gets excited by the flash. The resultant pressure traces are similar to Fig. 10a. The induction time is slightly longer and the peak pressure slightly lower, corresponding now to exactly the reflected C-J pressure. In Fig. 10c, all but 1 cm of the central part of the explosion tube is masked off by aluminum foil from the flash. The induction time now is lengthened to about 650 μsec. The pressure traces are similar to that of Fig. 10b and the amplitude again corresponds to the exact value for a reflected C-J detonation wave. These experiments indicate that detonation initiation can be achieved with only 1 cm length of the explosion tube excited by the flash.

A series of experiments were next performed to look at the effect of the size of the volume excited on the magnitude of the explosion pressure. With an explosion tube of 16 cm long, which corresponds exactly to the length of the flash tube itself, the pressure rise indicated a fully developed C-J detonation occured inside the excited volume of 16 cm. The induction delay time to explosion is about 440 μsec (Fig. 11a). With the length of the explosion tube reduced to 10 cm, the delay time has lengthened to 750 μsec. The pressure amplitude now drops to about 60% of the reflected C-J pressure of Fig. 11a (or Fig. 10a, 10b, 10c). A slow and quite small pressure rise is now observed prior to the sudden jump indicating the onset of detonation (Fig. 11b). When the length of the explosion tube is further reduced to 4 cm, the delay time to explosion is further lengthened to about 900 μsec. The pressure amplitude is now only about 50% of the reflected C-J pressure (Fig. 11c). These sets of experiments suggest that

there exists a critical volume where fully developed detonation can be formed. Below this critical volume the process does not yield a fully developed detonation wave. It appears that what happens inside the excited volume during the induction period is the formation of pressure waves due to in-homogeneities (perhaps due to non-uniform excitation or gas concentration fluctuations). These pressure waves propagating in the excited volume rich in free radicals, can easily lead to fully developed detonations. However, the development to detonation from these waves still requires finite time (or equivalently a finite travel). Thus, if the excited volume is too small, the detonation is not developed and the pressure rise is accordingly lower than the C-J value.

The important conclusion from these experiments is that detonation in hydrocarbon-oxygen or air mixtures can readily be initiated using a UV flash for dissociation and thus generating the necessary free radicals. Fully developed C-J detonation can be formed within this excited volume if the volume is above a certain critical size of the order of a few centi-meters. Due to the existence of free radicals ahead of the detonation wave propagating in the excited volume, the wave may become overdriven. The resultant pressure rise can exceed that of the C-J values for the mixture.

3. Calculation of Induction Time

In terms of the single event third generation FAE, the induction time to explosion is perhaps one of the most important parameters determining the effectiveness of such a weapon. If the induction time is too short then the free radical production via catalytic reactions will peak before the fuel and the ambient air have managed to mix to explosive proportions over any extent of the vapor cloud. On the other hand, if the induction time is overly long then the fuel-air mixture can completely disperse to below the detonability limits. Therefore, in the effective design of any

specific FAE device the induction time for a given catalyst fuel-air system
ideally should be matched to the time scale for fuel dispersion and air
mixing to explosive proportions over most of the vapor cloud. This implies
a judicious choice of a suitable catalyst-fuel-air combination. Unfortunately,
at the present time one does not know a priori the induction time for any
such arbitrary combination. However, in the light of the experiments des-
cribed in the previous section it is evident that there exists an intimate
link between the induction time and the initial free radical concentration.
Since the free radical concentration is in turn determined by the flash
intensity or by the catalyst concentration in catalytic initiation, the in-
duction time can thereby be linked to these most fundamental properties of
the primary initiating source. The establishment of a quantitative link
between the catalyst concentration and the induction time would provide the
criterion for the suitable choice of a catalyst for a given fuel-air system.

In the present program an attempt was made to investigate the
intricacies of such a quantitative link by theoretical modelling of the
chemico-kinetic processes for one fuel-oxidizer system. The gaseous explo-
sive studied was the equimolar H_2-Cl_2 system because of the availability
and relative simplicity of the chemical kinetic steps. It was felt it
would provide the maximum insight with minimum complexity and it also would
provide theoretical guidelines to assist in the interpretation of further
experiments which were carried out largely with this mixture. The basic
premise of the theoretical model is that at time t = 0, an initial concen-
tration of free radicals, atomic chlorine [Cl] in this case, is instan-
taneously produced by photodissociation in a constant volume explosive
H_2-Cl_2 gaseous medium. The induction times are then calculated from the
chemical kinetic scheme for the H_2-Cl_2 system using the reaction rate
constants for non-excited energy states[15]. In the present study, eight
initial free radical [Cl] concentrations were assumed arbitrarily in an

equimolar H_2-Cl_2 medium at 100 torr initial pressure to correspond roughly to a degree of dissociation of the Cl_2 ranging from about 0.2% to 50%. The chemical kinetic scheme used for the H_2-Cl_2 reaction is listed below.

$$Cl_2 + h\nu \xrightarrow{\ k_0\ } 2Cl$$

$$HCl + M_1 \xrightleftharpoons[k_1']{k_1} H + Cl + M_1$$

$$M_1 = H, Cl, H_2, Cl_2, HCl$$

$$H_2 + M_2 \xrightleftharpoons[k_2']{k_2} 2H + M_2$$

$$M_2 = Cl, Cl_2, HCl$$

$$H_2 + M_3 \xrightleftharpoons[k_3']{k_3} 2H + M_3$$

$$M_3 = H_2$$

$$H_2 + M_4 \xrightleftharpoons[k_4']{k_4} 2H + M_4$$

$$M_4 = H$$

$$Cl_2 + M_5 \xrightleftharpoons[k_5']{k_5} 2Cl + M_5$$

$$M_5 = HCl, H, H_2, Cl_2$$

$$Cl_2 + M_6 \xrightleftharpoons[k_6']{k_6} 2Cl + M_6$$

$$M_6 = Cl$$

Nernst Chain
$$\begin{cases} H + Cl_2 \xrightleftharpoons[k_7']{k_7} HCl + Cl \\[2ex] H_2 + Cl \xrightleftharpoons[k_8']{k_8} HCl + H \end{cases}$$
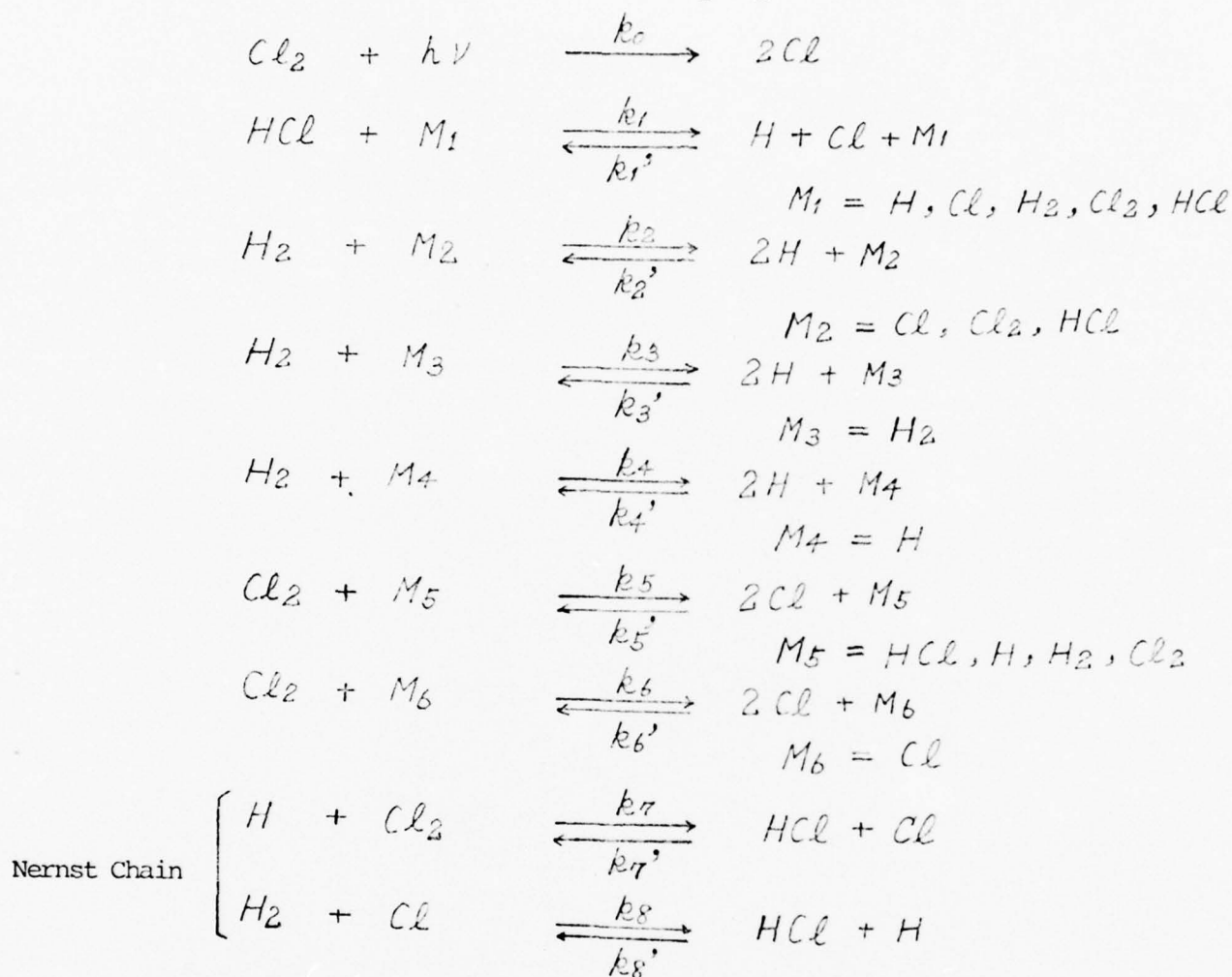
The constant volume explosion relations are

$$P = GRT$$

$$G = \sum C_i$$

$$\frac{dC_i}{dt} = f_i(C_j, T)$$

$$\frac{dh}{dt} = \frac{1}{\rho} \frac{dP}{dt}$$

$$h = \sum_{i=1}^{m} \frac{C_i \hat{h}_i m_i}{\rho}$$

$$\left(\sum_{i=1}^{m} C_{vi} \cdot C_i \right) \frac{dT}{dt} = \sum_{i=1}^{m} f_i (C_j, T) \cdot RT - \sum_{i=1}^{m} f_i (C_j, T) \hat{h}_i m_i$$

where P is the pressure in atm

R is the universal gas constant

C is the total concentration of chemical species

C_i, C_j are the concentration of species mole/liter

ρ is the density grams/liter

m_i is the molecular weight grams/mole

i are the species H_2, Cl_2, HCl, H, Cl

$\hat{h}_i$ is the species enthalpy cal/gm

h is the total enthalpy

The above chemical kinetic scheme in conjunction with the governing equations of constant volume explosion were solved numerically using the R-K-G method. H_2 and Cl_2 concentrations have been eliminated by the atom conservation laws. Chemical kinetic rates have been obtained from the data of Cohen et al[15]. From the above data and the JANAF tables, the backward reaction rates have been expressed in the Arrhenius form, namely $k = AT^n$ exp $(-E/RT)$. C_{p_i} and $\hat{h}_i$ have been expressed in terms of 6th and 5th order polynomials, respectively. For C_{p_i} polynomial coefficients have been calculated for ranges 298°K-2000°K and 2000°K - 4000°K.

Typical results for the production of H, Cl and HCl and the dis-
appearance of H_2 and Cl_2 are displayed for five cases in Figs. 12-17 which
shows the concentration of each species as a function of time. The initial
condition in each case is the assumed chlorine atom concentration [Cl] at
t = 0 produced non-thermally due to the photodissociation of chlorine mole-
cules. The chlorine atoms are then consumed in the Nernst chain mechanism
producing hydrogen atoms and hydrogen chloride. At the same time the
temperature is increasing due to the exothermic production of hydrogen
chloride eventually to exceed the auto-ignition limit for the mixture. The
corresponding temperature-time curves are displayed in Figs. 18-23. Thus
after passing the minimum point in the initial phases of the reaction the
chlorine atom· concentration is replenished thermally due to the exother-
micity of the combustion process. In the present study, the induction time
is defined as the time at which the temperature of the medium begins to
increase sharply. The actual value is established by taking the intercept
of the tangent to the maximum slope of the temperature-time curve with the
initial temperature line (298°K). The induction times so calculated are
plotted in Fig. 24 against the initial chlorine atom concentration [Cl]
seeded. The degree of dissociation of the Cl_2 molecule equivalent to this
is also indicated on the abscissa. It can be observed that at high seeded
chlorine atom concentration corresponding to about 50% Cl_2 dissociation,
the induction time is very short (<1 μsec in this case). Over quite a wide
range of decreasing initial chlorine atom concentration (corresponding
roughly to degrees of dissociation of Cl_2 between 50% - 1% respectively)
the induction time increases relatively gradually. However, for still lower
initial chlorine atom concentration the rate of increase in the induction
time accelerates sharply in a way that is qualitatively similar to the
sharp increase in induction time for thermal ignition as the auto-ignition
limits are approached. In this case one can therefore think of some limit-

ing non thermal ignition criterion analogous to that based on temperature for thermal ignition where now for non-thermal ignition, the criterion would be based on some critical limiting value of the initial radical concentration. Every catalyst-fuel-oxidizer can therefore in principle be characterized by some critical minimum initial radical concentration for non-thermal ignition analogous to the characteristic auto-ignition temperature for thermal ignition. As a basis for further comparison between the non-thermal and thermal modes of ignition, two cases of thermal ignition have also been calculated theoretically in the present work. The basic premise of the theoretical model for thermal ignition is that an H_2–Cl_2 equimolar gas mixture, initially at 100 torr and 298°K, is heated up instantaneously at $t = 0$ to a higher temperature (1400°K and 1800°K in this case). The same chemical kinetic scheme as before has been considered in the calculations of the induction time, except that now the initiating step at a very early time is the thermal dissociation of the chlorine molecules. This process triggers the Nernst chain of reactions where now the chemical kinetic rates of the Nernst chain have been extremely accelerated due to the higher temperatures. Figs. 25 and 26 show that the production rate of hydrochloride [HCl] increases drastically after about the first microsecond or so. Beyond that, howerver, the Nernst chain scheme becomes quite dominant in the production of [H] and [Cl]. In fact one can say that the chain reactions determine the entire combustion process in thermal ignition. This is quite distinct from the photochemical ignition where the [HCl] dominates the kinetic processes at all times. The induction times for the two cases of thermal ignition have been determined from the temperature-time curves displayed in Figs. 27 and 28 as before. In order to further elucidate the distinction between the thermal and photochemical ignition, the results of the present calculations have been replotted in Fig. 29 in the well-known phase plane discussed by Berlad[16] and Cerkanowicz[13]. The curves show the progress of the reactions for each mode of initiation and each curve approaching its own final state. One

can clearly see the distinction between the thermal and the photochemical initiation delineated by the separation curve S. A final calculation was made to check the effect of initial pressure on the induction time for both the thermal and the photochemical modes of initiation. For the thermal mode of initiation, an instantaneous jump of temperature from 298°K to 1600°K was assumed; for the photolysis case radiation intensity of 1.5 kw/cm^2 at 3300 Å was taken. In all cases the explosive gas mixture was equimolar H_2-Cl_2 at initial pressures ranging from 20 to 760 torr. Fig. 30 displays the calculated induction times as a function of the initial pressure. The induction times in this case were calculated by two methods. One of these was as before from the maximum slope of the temperature-time curve; the other was by measuring the time for 10% HCl production of the total mole concentration. In all cases the induction times so calculated were within about 5% of each other. From Fig. 30 it is evident that for both thermal and photo-chemical ignition the induction time increases with decreasing initial pressure with the sharpest increase for initial pressures less than 100 torr. These curves are very compatible with the trend of ignition delay with pressure determined experimentally by Cerkanowicz[13] for the CH_4-oxidizer and the H_2-oxidizer systems. To compare the relative efficiency of photochemical versus thermal ignition, the data generated were normalized with respect to the induction time at 760 torr to make both modes of initiation compatible for comparison. The replotted normalized curve is shown in Fig. 31 from which it is seen that the induction times for photochemical initiation are much less than that for thermal, for decreasing initial pressure. Since the induction time is a direct measure of the efficiency of the reaction itself (the shorter the induction time, the more efficient the reaction), the results indicate that in terms of efficiency, photochemical initiation is much more efficient than thermal initiation which is not an unexpected conclusion just from simple thermo-

dynamic considerations. In fact, Cerkanowicz[14] has demonstrated experi-
mentally that the relative minimum energy required for ignition of sub-
atmospheric methane-air mixtures is much less with photochemical than with
spark (thermal) ignition. The results of the theoretical calculations can
be summarized as follows. A critical limiting value of the initial free
radical concentration in a typical catalyst-fuel-oxidizer medium for photo-
chemical initiation of explosive reactions can be defined to characterize
the ignition limits for this mode of initiation. This is analogous to the
auto-ignition limit for the thermal mode of initiation. The induction
times for the initiation of explosive reactions by photochemical means are
very distinct from those by thermal means. Moreover, the results of our
work as well as the work of Cerkanowicz indicates that photochemical ini-
tiation is much more efficient than thermal initiation of explosive reac-
tions in the same gaseous medium.

4. Wave Processes During Photochemical Initiation

Although from the experiments described in Section 2 of this
report we could confidently conclude that detonative combustion could be
produced directly by photochemical means we could not, because of the
nature of the experimental apparatus, look directly at the nature of the
wave phenomena during the photochemical initiation process. Pressure
measurements in the explosion cell suggested that the pressure level
achieved was somewhat in excess of the C-J level corresponding to the
initial conditions of the particular medium. A C-J detonation wave, however,
was observed to emanate from the ignition cavity, suggesting that some sort
of transient wave interaction phenomena must have been occuring in the
explosion cell. At this point it was felt necessary to design an experi-
ment which would permit direct observation of these effects while preserving
the overall similarity of the photochemical initiation system. Since we

had available some rectangular UV transmitting quartz plates, 75 mm x 150 mm x 6 mm thick, the concept for the experiment was to construct a rectangular quartz chamber from four such plates as illustrated in Fig. 32. This yielded a chamber which was 75 mm x 75 mm in square cross-section and 15 cm long and which was irradiated by two xenon flashlamps (Xen. Corp. FPA-8-100C) placed adjacent to two opposite quartz plates. The irradiation of the inside of the explosion chamber was enhanced by the addition of parabolic reflectors which redirected as much of the flashlamp output as possible back into the chamber. Observations of phenomena inside the explosion chamber were made optically by spark schlieren photography through the other pair of windows and orthogonal to the direction of UV irradiation. In this way the effect of the intense flash background illumination was minimized since it otherwise would have completely overwhelmed the schlieren field illumination if viewed directly. The sequence of events inside the explosion chamber were reconstructed from single spark schlieren records of individual shots, since the events were very reproducible. Complimentary measurements were also made simultaneously via calibrated pressure transducers inserted, as before, in the ends of the rectangular quartz explosion cell. Since the four quartz plates were held together with a stainless steel rib cage and "0" ring seals, the pressure transducers were obstructed from the direct flash UV irradiation. In fact they were about 10 mm beyond the edges of the quartz observation windows. For this very same reason, the total unobstructed view of 5 cm x 12 cm was available for schlieren observation.

To get some feel for the initial free radical distribution in this apparatus, theoretical calculations, using the absorption spectrum of the Cl_2 molecule (Fig. 5) were made to estimate the degree of absorption of radiation within the span of the H_2-Cl_2 mixture at 100 torr initial pressure contained within the rectangular chamber. As illustrated in Fig.

33 the analysis assumes an intensity I_o of UV radiation centered around 3300 $\overset{o}{A}$ (which corresponds to the peak Cl_2 absorption) to irradiate from two sides the slab of gas contained between two UV transmitting windows. What is plotted here is the intensity of the radiation field inside the slab of gas normalized against the initial intensity I_o of the irradiating flash. The results indicate that we would get significant absorption in the span of gas confined within the two quartz windows with only 21% of the total incident radiation intensity penetrating to the center of symmetry of the chamber. This would imply a peak free radical concentration immediately adjacent to the windows, but also a substantially significant distribution throughout the entire volume. Fig. 34 illustrates a sequence of typical spark schlieren records of the photochemical initiation in this apparatus. In this case the flashlamps were masked at their ends leaving exposed the central 5 cm spans to guarantee spanwise uniformity of flash intensity. On the photographs the open spans of the flashlamps are between the two arrowlike black markers. The first thing to observe is that two discrete wave fronts originate from the vicinity of the windows through which the UV radiation is transmitted from the flashlamps. This is compatible with the fact that we expect the highest free radical concentration there and hence the region of the most intense chemical activity. The two discrete fronts advance on each other, diffracting at the edges of the non-irradiated region (the region outside the black markers) and colliding to form a Mach reflection which then moves outward longitudinally to impact on the end-mounted pressure transducers. The pressure records are displayed adjacent to the schlieren photographs. The first pulse corresponds to the EM noise generated by the energy discharge to the flash lamps from the low inductance condenser bank (8 µf, 18 kv corresponding to 1300 joules stored energy). The small fuzzy signal to the right of the first pulse is at the time that the schlieren spark source fires. The third peak is the pressure signal from the

calibrated (PCB 113A24) pressure transducer signalling the arrival of the wave at the ends of the explosion chamber. Not surprisingly, the pressure measured by the transducers corresponds to a level which is in excess of that for a C-J wave and can be attributed to the overdriven Mach stem. Thus, although supra-detonation pressures are produced as a result of wave interaction phenomena, one cannot say at this stage that the initial waves are detonations. No clear cut identification as such can be made from the multilayered wrinkled structure of the wave as it appears on the schlieren photographs. Wave velocity measurements over such a short span of travel are too inaccurate to give any meaningful estimations apart from being an insensitive means of assessment in the first place. To clarify this point, one of the flashlamps on one side of the chamber was completely masked out and the apparatus fired again under otherwise identical conditions. Fig. 35 now indicates the outward movement of one discontinuity only. In this case, the wave is free to traverse the entire chamber without interaction and the pressure record indicates first that its arrival at the transducer is later than before with a pressure level that is much below the C-J value. It was not clear at this stage whether the discontinuity was a deflagration wave driven by the exothermic combustion processes in its wake or an inert decaying shock wave (blast wave) produced by the rapid photochemical absorption of the flash energy in the vicinity of the quartz window. Fig. 36 shows a simultaneous schlieren photograph and pressure record of an identical flash in a medium of chlorine gas (Cl_2) alone. No wave phenomena are indicated in either the schlieren field or in the pressure record, confirming that the wave observed in the previous records (Fig. 35) could not be due to the radiation absorption process alone, but is rather due to combustion processes subsequent to photochemical ignition. The energy of the flash was increased to 2300 joules in an attempt to pump more UV radiation into the explosion chamber via the single unmasked flashlamp. Fig. 37 clearly indicates from the

schlieren photograph and the pressure, that direct initiation of detonation was produced in this case. The pressure level corresponds in this case identically to the C-J level. Although we had demonstrated unmistakably at this stage that direct initiation of detonation could be produced by photochemical means, it was intriguing to explore what sort of phenomena would be observed with even more intense UV irradiation. To this end, we removed all the masking to the flashlamps and proceeded to observe the phenomena with progressively increasing flash energy beyond that necessary for the direct initiation of detonation. Fig. 38 illustrates such a sequence of experiments in which the flash energy increases as one goes from top to bottom of the series of photographs. The black arrow-like marker indicates the center of the appartus. Because of the non-uniformity of the span wise intensity of the flashlamps, totally unmasked here, one immediately notices the wavy spanwise contours of the waves. There are two observations that must be made about the results displayed in this figure. The first is that there is a progressive fading or "washing out" of the detonation front discontinuity in the schlieren field. This is coupled with a measurable drop in the pressure jump across the detonation front even though the detonation velocity is maintained. We can attribute this to pre-dissociation and the associated increase in the acoustic speed in the intensely irradiated gas ahead of the advancing detonative front. In fact, by progressively increasing the flash energy, we expect that the pressure behind the discontinuity can be made to range from the C-J level to that corresponding to constant volume explosion of about half C-J level. This corresponds to the situation where the discontinuity has degenerated to an acoustic level in terms of the pressure jump as it propagates into a highly dissociated gas. To all intents and purposes, the entire medium would be reacting throughout more or less volumetrically at this supra-level of UV irradiation. The important conclusions that can be drawn from this series of experiments can be summed up as follows. The region of highest

free radical concentration is immediately adjacent to the windows through which the medium is irradiated by UV radiation. This is confirmed by the fact that the discrete combustion wave discontinuities originate from these regions. Direct initiation of detonation in the explosion chamber can be produced photochemically when the flash intensity exceeds a certain critical intensity. Detonations can also be produced in short order within the explosion chamber by the Mach collision of deflagration waves generated at sub-critical flash intensities. At intensity levels of irradiation in excess of that necessary for direct initiation, there is a progressive weakening of the detonation discontinuity as the wave now propagates into a highly pre-dissociated medium. It is expected that with supra-intense irradiation, volumetric initiation of chemical reactions throughout the entire medium would be produced.

5. Mechanisms of Photochemical Initiation of Detonation

Although we could now see the presence of the detonation right in the rectangular explosion chamber, we still could not trace its development from the instance of the first appearance of chemical reactions. This is because in the latter experiments, the region immediately adjacent to the window is still obscurred by the bracket hinges holding the chamber in a sealed configuration. Once again it was necessary to modify the apparatus so that the field of view including the entire flow field from the window out could be visible. Having demonstrated that a single flashlamp will do the job of initiating a detonation wave in an equimolar H_2-Cl_2 mixture at a 100 torr, in the modified apparatus we placed a single flashlamp adjacent to a quartz window inserted inside a cylindrical chamber such that now the entire flow field was visible by schlieren photography. A sketch of the arrangement is shown in Fig. 39. The quartz window aperture was 35 mm in diameter and 6 mm thick illuminated by a single xenon flashlamp (Xen. Corp. FPA-8

--100C) placed about 30 mm away. The explosion chamber was a stainless steel cylinder 100 mm in diameter and 100 mm long, equipped with large windows (100 mm diameter) through which schlieren observation of the entire explosion chamber could be made, including an edge-on view of the quartz initiating port window. A pressure transducer (PCB113A24) was mounted at the opposite end of the explosion chamber facing the initiating port. Fig. 40 displays the range of combustion phenomena produced in such an apparatus via photochemical initiation with progressively increasing flash energy. The mixture composition in all cases here is equimolar H_2-Cl_2 at 100 torr initial pressure with the flash energy ranging from 5500 joules to 7000 joules through the single xenon flashlamp. The late time appearance in these photographs corresponds to three distinct propagation regimes very reminiscent of those observed in the thermal blast initiation mode[4], namely the deflagrative, transitional and detonative regimes of propagation. However, here the similarity ends since a closer examination of the detailed sequence of steps during the initiation process clearly indicates a drastically different mechanism of initiation. For example, Fig. 41 displays a detailed sequence of the development (from left to right) of the combustion wave in the deflagrative mode of propagation at time intervals approximately 5 μsec apart. We note that the combustion phenomena starts with a diffuse region of chemical reactions immediately adjacent to the irradiating quartz window. This is followed in short order (frame 4) by the rapid development of a shock wave which ultimately in late time leads to the development of a deflagration wave. It must be emphasized that the mechanism here in photochemical initiation is drastically different from that for thermal initiation such as in the blast initiation mode. In the photochemical initiation situation the shock wave and the subsequent deflagration wave are formed solely as a result of the exothermic processes in the gas after the initiation of chemical reactions. In the blast initiation mode, auto-ignition and subsequent non-

linear coupling between chemical kinetics and non-steady gas dynamics in the
wake of a decaying blast wave constitute the mechanism of initiation. Refer-
ring back now to the photochemical initiation of the transitional regime of
propagation displayed in Fig. 42, one sees again the diffuse region of chemi-
cal reactions (frame 1) followed by the rapid development of a precursor shock
front (frame 2). However, in this case one also notices the development of
a detonation bubble (frame 3) which subsequently sweeps around and engulfs
the entire shock sphere resulting ultimately in a full-fledged detonation wave.
Fig. 43 displays a sequence of spark schlieren photographs illustrating the
direct initiation of detonation by photochemical means. Here the shock wave
evolves very rapidly and a full-fledged detonation is seen to propagate out
right from the very first frame. The reason for the double humped initial
shape of the detonation front is due to the additional radiation reflected
into the explosion chamber along the walls of the tube holding the UV radia-
tion transmitting quartz window. The tube was wrapped with aluminum foil to
prevent transverse transmission of UV light into the edges of the explosion
chamber and it seems it acted as an ideal reflector of specular radiation
into the chamber through the quartz window. To the best of our knowledge,
the sequence of photographs displayed in Figs. 40-43 are the first ever il-
lustrating the detailed mechanism of initiation of detonative reactions via
the free radical initiation mode using photo-dissociation in the present case.
Pressure measurements carried out under various conditions of initiation are
displayed in Fig. 44. Here we plot reflected pressure against initial pres-
sure of the equimolar H_2-Cl_2 mixture. The yardstick that we take for compari-
son here is the pressure measurements obtained in a 1 meter long tube ini-
tiated by a spark at one end. The detonation pressure here corresponds to
the classical C-J value. Spark ignition was also done in the cylindrical
chamber right on the face of the quartz window. Here the pressures measured
are very scattered and all in excess of the C-J level. We attribute this

to the fact that because of the short span available for the travel of the diverging hemispherical wave (<100 mm) its propagation was still influenced partly by the spark source energy and it was still in the overdriven state. The case for direct photochemical initiation in the present apparatus corresponds roughly to 600 joules (8 μf, 12 kv) of flash energy for 100 torr initial pressure in equimolar H_2-Cl_2. The reflected detonation pressure at this level of flash energy for a range of initial pressures falls consistently below that for a spark (thermally) initiated detonation in a tube. At higher flash energy, the results show an even lower reflected detonation pressure significantly below the C-J value. Even with a longer flash duration the reflected detonation pressure is still maintained below the C-J level. As in the previous case, we attribute this decrease in the detonation pressure to the fact that the wave is propagating with a partially predissociated medium with an increased acoustic speed. In fact, a number of experiments were performed using the long duration flash for photochemical initiation in a C_2H_2-O_2 mixture weakly sensitized with NO_2. Fig. 45 illustrates a very intriguing sequence of photographs with a flash energy of 3250 joules (2250 μf, 1.7 kv) where we see a diffuse region of chemical reactions develop into a discrete front. The interesting feature here is that the front is propagating at something like 100 m/sec, i.e., subsonically. Hence the wave cannot sustain a shock yet it is awfully fast for a flame. Although we have not yet fully resolved the true character of the wave in this case, we feel that it may be a laminar flame propagating into a chemically pre-activated medium. At a higher flash energy of 7000 joules (2250 μf, 2.5 kv) Fig. 46 displays a more wrinkled flame surface propagating at 140 m/sec. The interesting thing is that upon reflection of this supposedly shockless flame front from the opposite wall where the pressure transducer is located, reflected pressure levels of the order of the C-J detonation level are recorded. This certainly is a novel phenomenon that merits further investigation.

The main conclusions that may be drawn from this set of experiments can be summarized as follows. Depending on the flash energy photochemical initiation can produce three distinct late time regimes of propagation analogous to those observed with the blast initiation mode. However, results show that the mechanisms for the two modes of initiation are drastically different. In the blast mode, the initiation process is controlled by the autoignition and non-linear coupling of chemical kinetics and transient gas dynamics in the wake of a blast wave generated by the source. In the photochemical initiation, it is via the production of a shock wave from the exothermicity of the chemical reactions triggered by the free radicals. The results also show that for flash energies in excess for that necessary for direct initiation of detonation by photochemical means, the strength of the detonation wave decreases progressively with increasing flash energy. We can attribute this to the chemical pre-activation via dissociation of the gaseous explosive medium ahead of the advancing detonation front.

6. Conclusions

The results of the present study demonstrate conclusively the feasibility of initiation of detonation in gaseous explosive media via the free radical mode of initiation. Direct initiation of detonation has been achieved after a characteristic induction time provided the initial free radical concentration exceeds a certain minimum critical value. These conclusions are based on the present experiments performed using flash photolysis as the radical producing technique in mixtures of H_2-Cl_2 and $C_2H_2-O_2$ with and without NO_2 sensitization. The experimental results also indicate that the induction time for the evolution of detonative combustion depends on the initial free radical concentration. Theoretical calculations show that the induction time for explosive chemical reactions increases with decreasing initial free radical concentration. The rate of increase is

very sharp when a critical minimum limiting value of the initial free
radical concentration is approached. This suggests that an ignition criterion,
similar to the temperature auto-ignition limit in thermal ignition, can be
evolved for photochemical initiation based on this minimum initial free
radical concentration. The results also indicate that the induction times
for the initiation of chemical reactions by photochemical means are very
distinct from those by thermal means due to the difference in the predomi-
nance of the chemical kinetic steps in the two modes. Relative comparison
of the two modes of initiation indicates that photochemical initiation is
more efficient than thermal initiation. An experimental study of the mecha-
nisms of photochemical initiation of detonation indicate that discrete dis-
continuous combustion waves are produced in the regions of highest free radi-
cal concentrations in the explosive medium. The highest concentrations occur
in samples of the explosive gas closest to the UV irradiating source and
hence these wave fronts originate there. However, significant absorption also
occurs ahead of the advancing fronts so that the combustion waves are propa-
gating into a medium which already chemically preactivated by dissociation.
Detonations are produced directly in excess of some critical level of flash
intensity or can develop very rapidly by the Mach collision of deflagration
waves generated by sub-critical flash intensities. In the photochemical ini-
tiation process the combustion phenomena start with a diffuse region of
chemical reactions in the vicinity of the highest free radical concentration,
adjacent to the UV irradiating quartz windows in the present case. This is
immediately followed by the rapid development of a shock wave which ultimately
can lead to the development of either the deflagrative, transitional or
detonative late time regimes of propagation. These regimes are reminiscent
of those produced via the blast (thermal) initiation mode. However, it
must be emphasized that the mechanisms here in photochemical initiation are
drastically different from those for the blast mode of initiation. By

mechanisms we mean here the detailed sequence of events between the triggering of the phenomenon to the evolution of the full-fledged combustion wave. In the photochemical initiation situation, the shock wave and the subsequent combustion wave are formed solely as a result of the exothermic processes in the gas after the initiation of chemical reactions due to the introduction of the free radicals. In the blast initiation mode, auto-ignition and subsequent non-linear coupling between chemical kinetics and transient hydrodynamics in the wake of the decaying blast wave constitute the mechanism of initiation. To the best of our knowledge the results of the present study are the first ever to elucidate in detail the mechanisms of photochemical initiation of detonation. Finally, the results also show that for flash energies (and hence initial free radical concentrations) in excess of that necessary for direct initiation, the strength of the detonation wave decreases progressively with increasing flash energy. We can attribute this to the chemical pre-activation via dissociation of the gaseous explosive medium ahead of the advancing detonation front. It seems reasonable to expect that with supra-intense irradiation, volumetric initiation of chemical reactions throughout the entire medium would be achieved.

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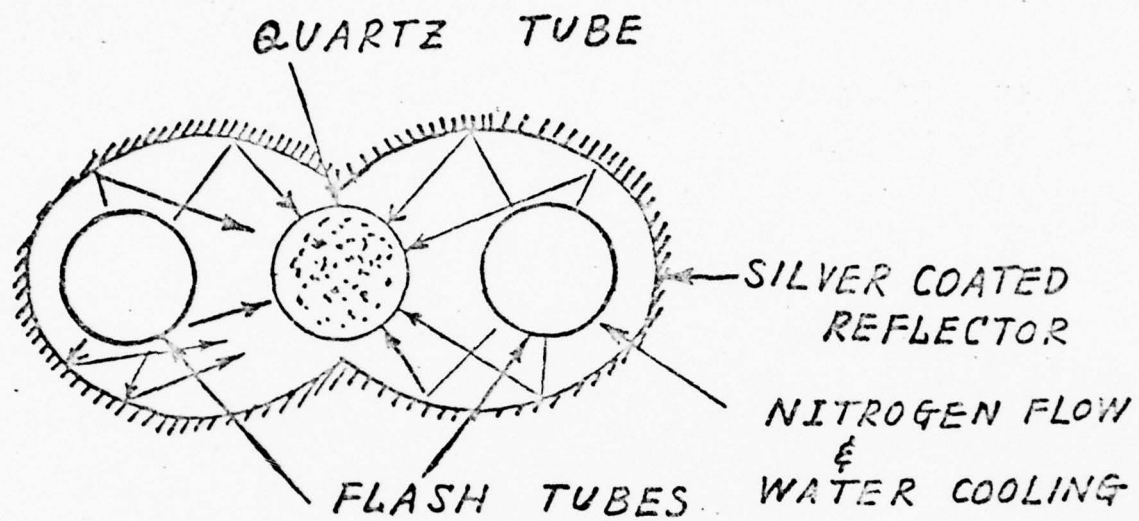
FIG·I PHOTOCHEMICAL INITIATION OF DETONATION IN A MODIFIED LASER CAVITY

Water - Cooled
EG&G FX-47C
Xenon Flashlamps
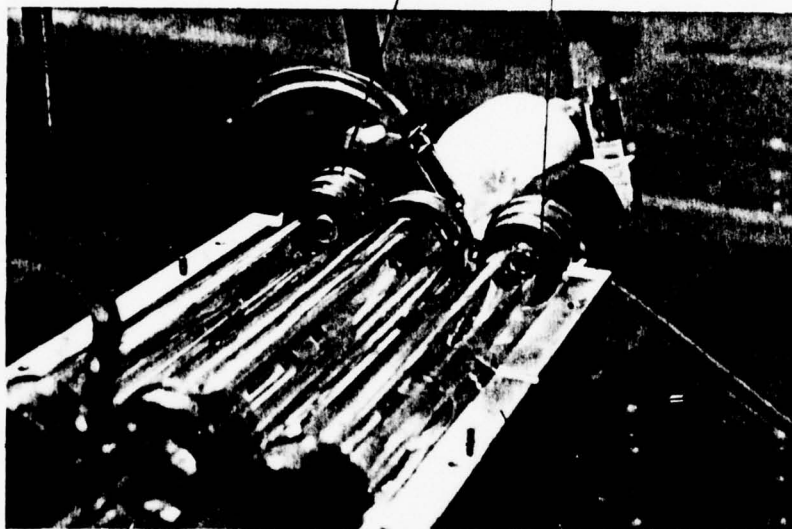
Water - Cooled
Explosion Tube

Lower Half of
Flash Cavity

FIG·2 CLOSEUP VIEW OF FLASH CAVITY

Explosion Tube Extension

Upper Half of Double-Elliptical
Silvered Flash Cavity
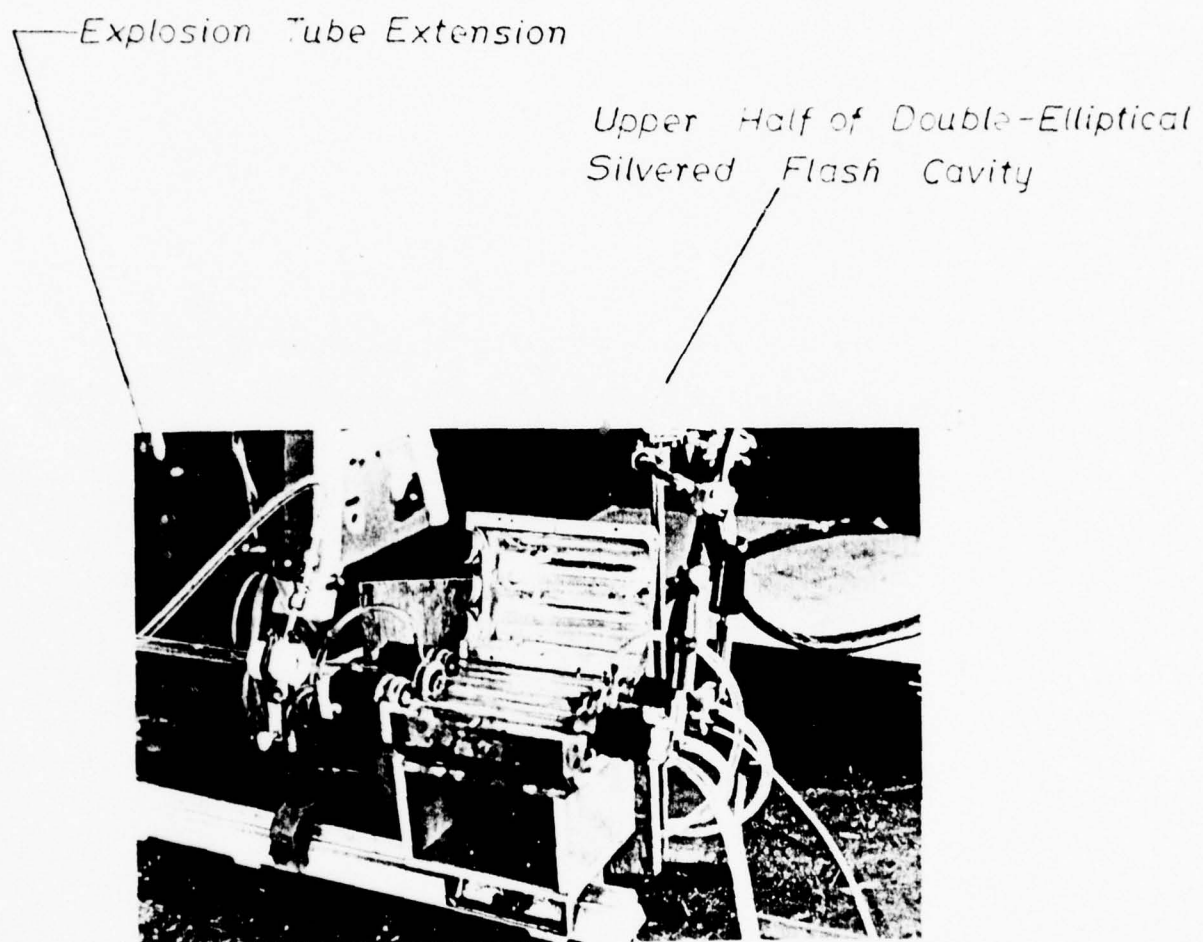
FIG·3   OVERALL VIEW OF FLASH INITIATION
APPARATUS
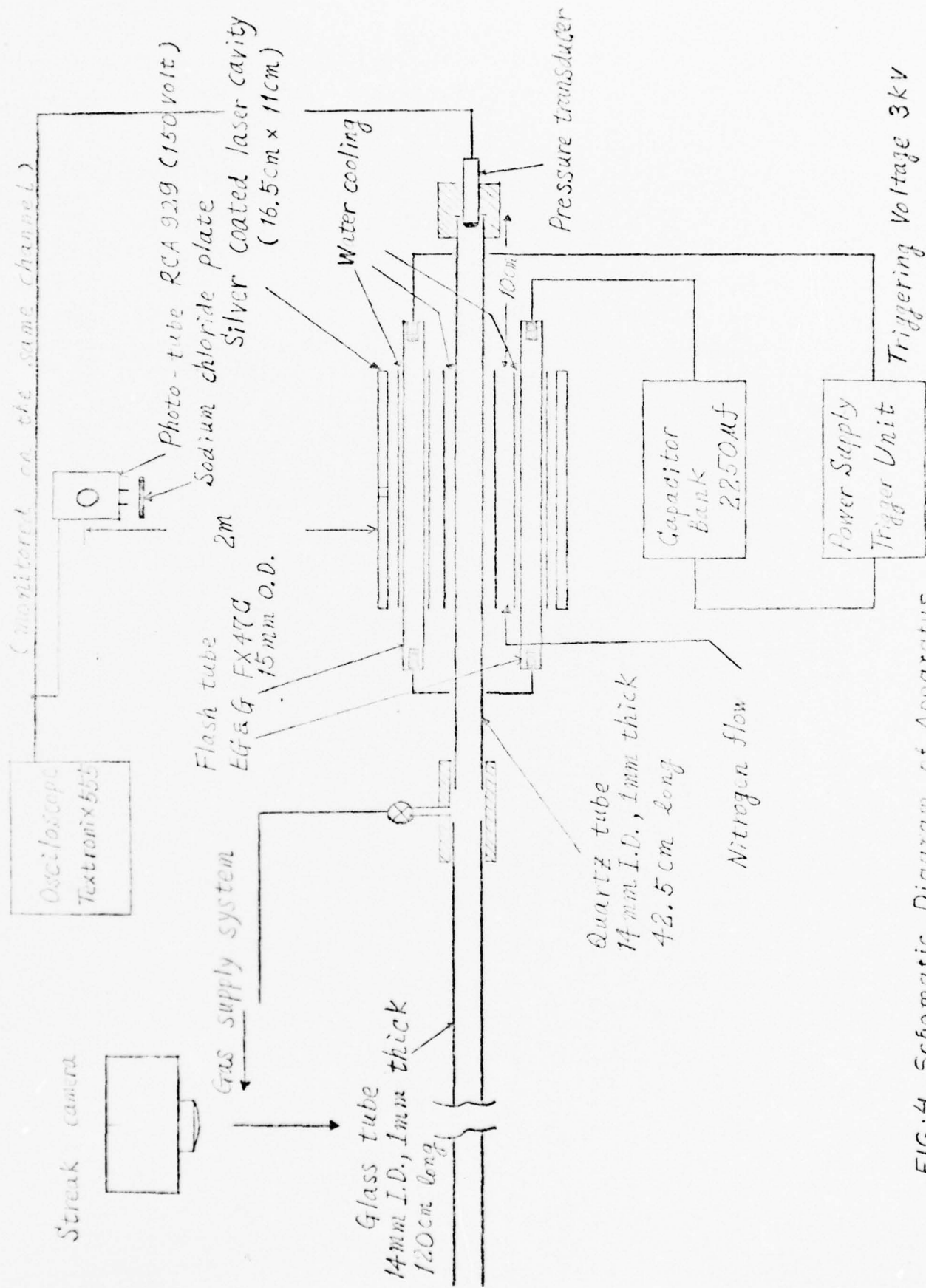
FIG·4 Schematic Diagram of Apparatus

Streak camera

Oscilloscope
Textronix 555

(Monitored on the same channel)

Gas supply system

Glass tube
14 mm I.D., 1mm thick
120 cm long

Photo-tube RCA 929 (150 volt)
Sodium chloride plate
Silver coated laser cavity
(16.5cm × 11cm)

Flash tube
EG&G FX47C
15mm O.D.
2m

Water cooling

Pressure transducer

10cm

Quartz tube
14 mm I.D., 1mm thick
42.5 cm long

Nitrogen flow

Capacitor
Bank
2250 Mf

Power Supply
Trigger Unit

Triggering Voltage 3 kv

Absorption Spectra of Cl_2 and NO_2

$$I = I_0 \, 10^{-\epsilon c x}$$

$$NO_2 + h\nu \longrightarrow NO + O$$
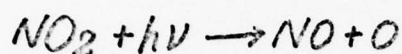
ϵ : liter / mole / cm
c : mole / liter
x : cm

$$Cl_2 + h\nu \longrightarrow 2Cl$$
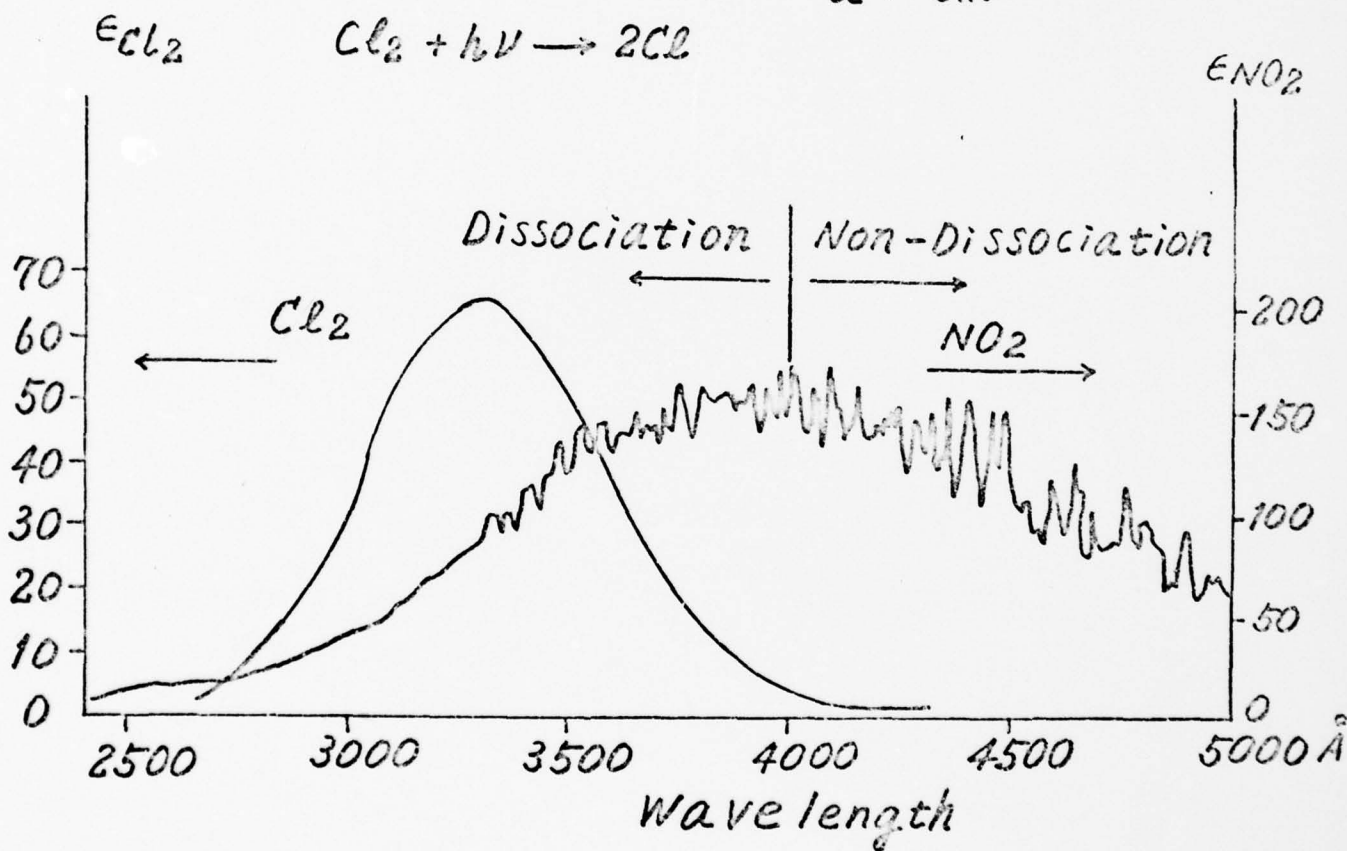
FIG·5   ABSORPTION SPECTRA OF Cl_2 AND NO_2

Explosive
Mixture : $95\% \left(C_2H_2 + O_2 \right) + 5\% NO_2$

$$P_0 = 100 \text{ torr}$$

Flash Energy :   6000 joules

t_i

$t = 0$

$\rightarrow t = 200 \, \mu \sec / div$
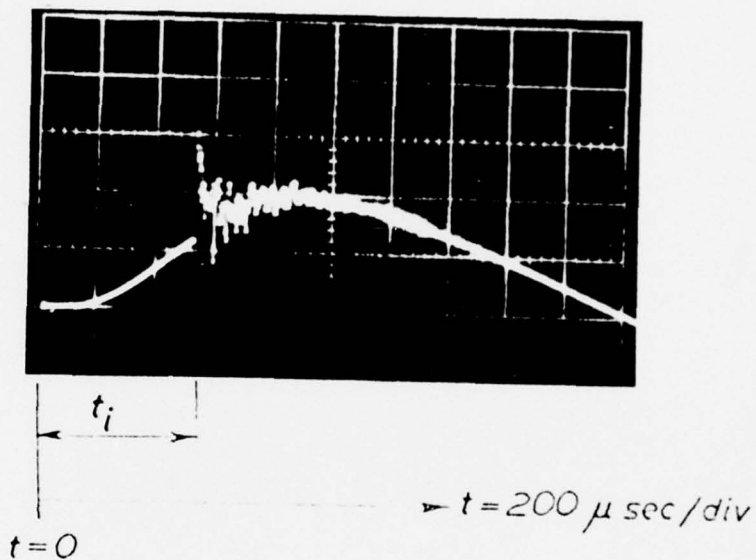
FIG. 6 Simultaneous Record of Flash
        Intensity and the Abrupt Pressure
        Rise in the Explosion Cavity after the
        Induction Time — t_i
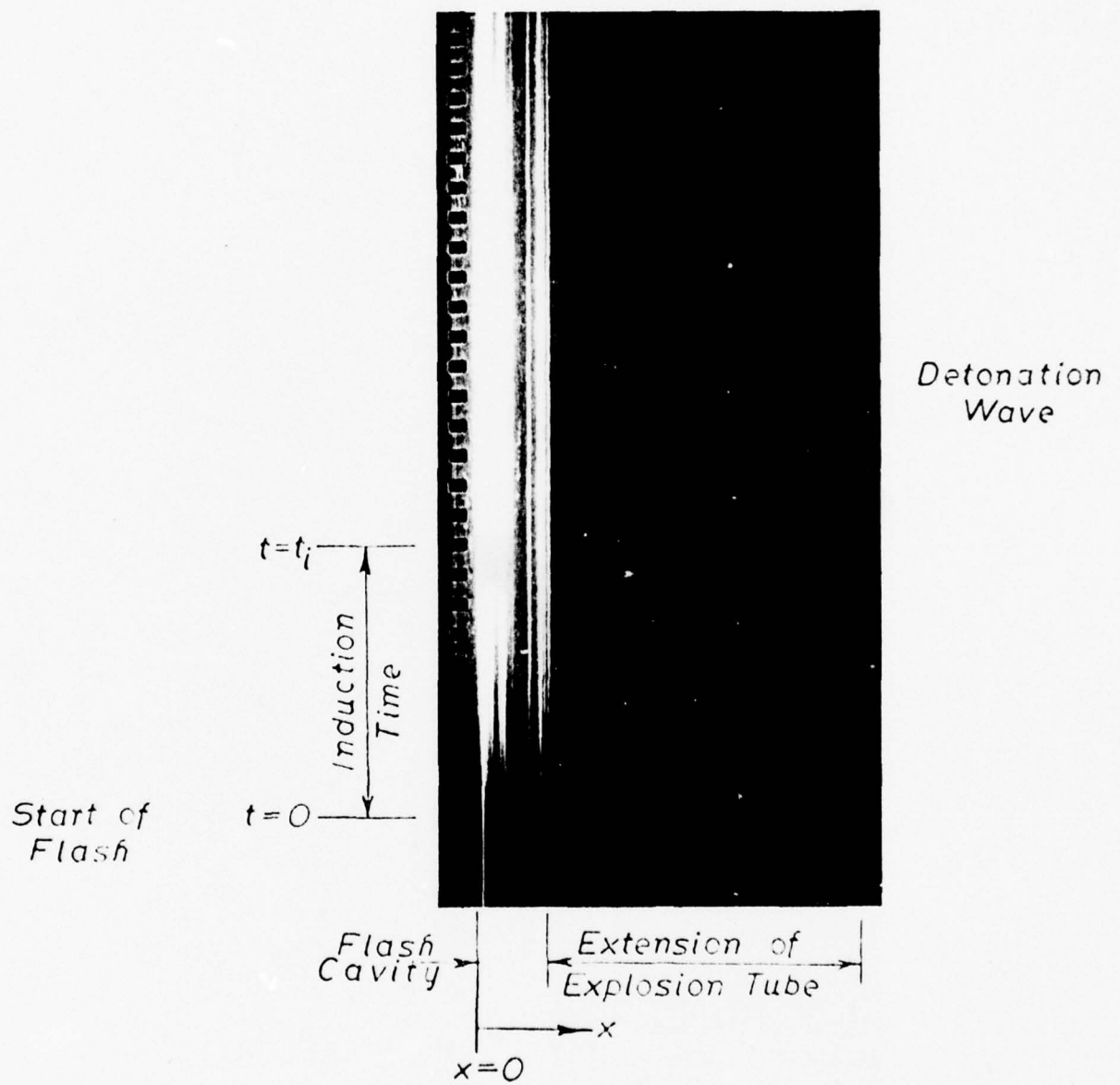
FIG. 7   STREAK   RECORD   OF FLASH
INITIATION   OF   DETONATION

VARIATION OF INDUCTION TIME

FIG. 8   VARIATION OF INDUCTION TIME WITH INITIAL PRESSURE

4.0 —

P_{40}, T_{40}	P_0, T_0

← shock wave

P_4, T_4	P_0, T_0

3.0 —

o $H_2 + \frac{1}{2} O_2 + 25\% NO_2$ $(\gamma = 1.212)$

● $H_2 + \frac{1}{2} O_2$ $(\gamma = 1.402)$

$(8.95, 9.62)$

$(9.10, 9.84)$ $(8.90, 11.1)$

$(P_4/P_{40} = 9.38, T_{4/40} = 10.25)$

2.0 —

$(8.72, 10.78)$ $(9.24, 10.03)$

$(P_4/P_{40} = 9.10, T_{4/40} = 11.46)$

$(8.26, 10.45)$

1.0 —

$$\frac{P_4}{P_0} \frac{\eta}{\gamma} \left[1 - \frac{(\gamma-1)}{\gamma+1} (1-\eta) \frac{C_0}{C_4} \eta^{-\frac{1}{2}} \right]^{\frac{2\gamma}{\gamma-1}} = \frac{2}{\gamma+1} \left(1 - \frac{\gamma-1}{2} \eta \right)$$

$\eta = 1/M^2$

$C;$ sound speed

P_{40}

0 —

| 100 | 200 | 380 | 760 | Torr. |
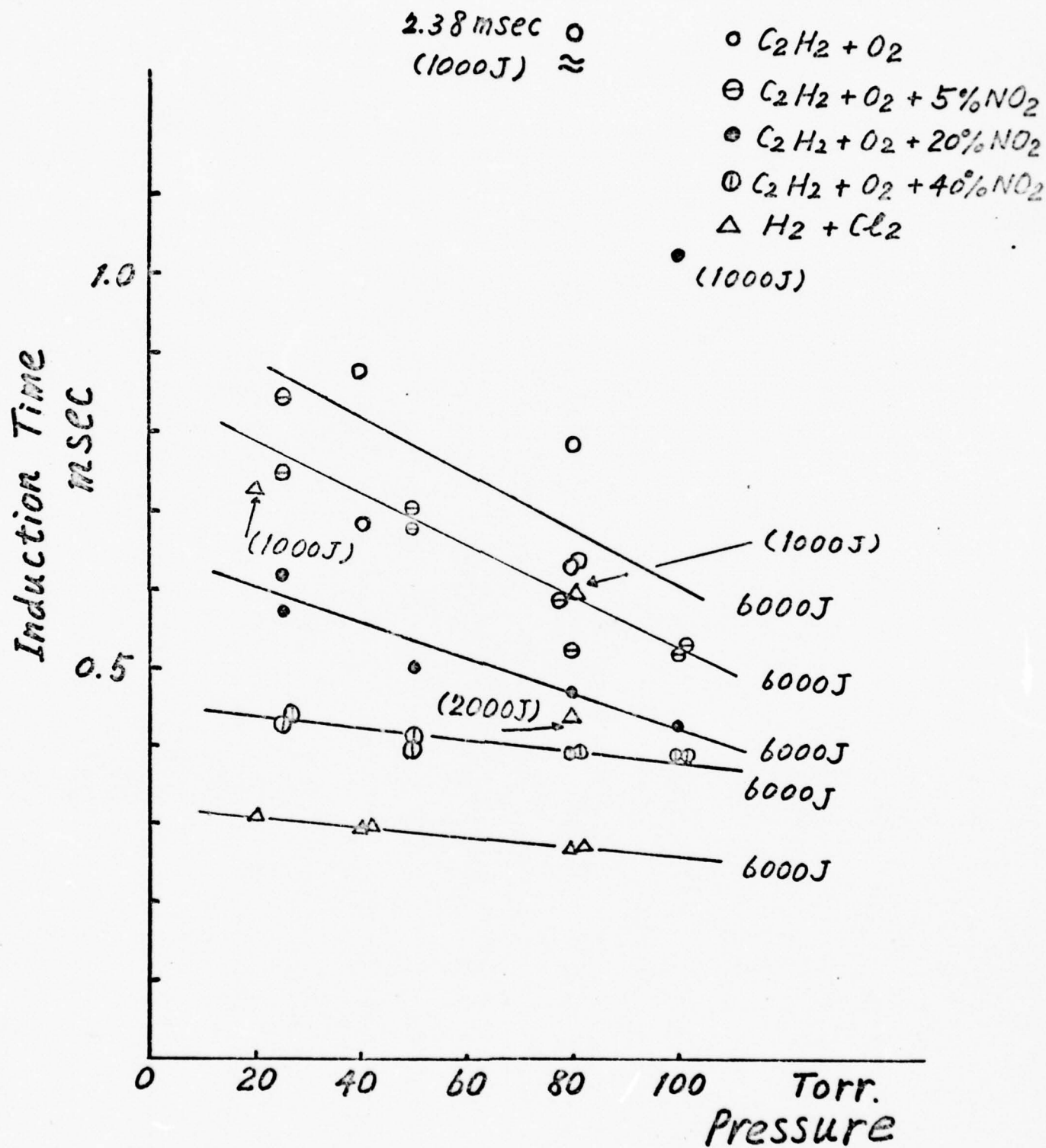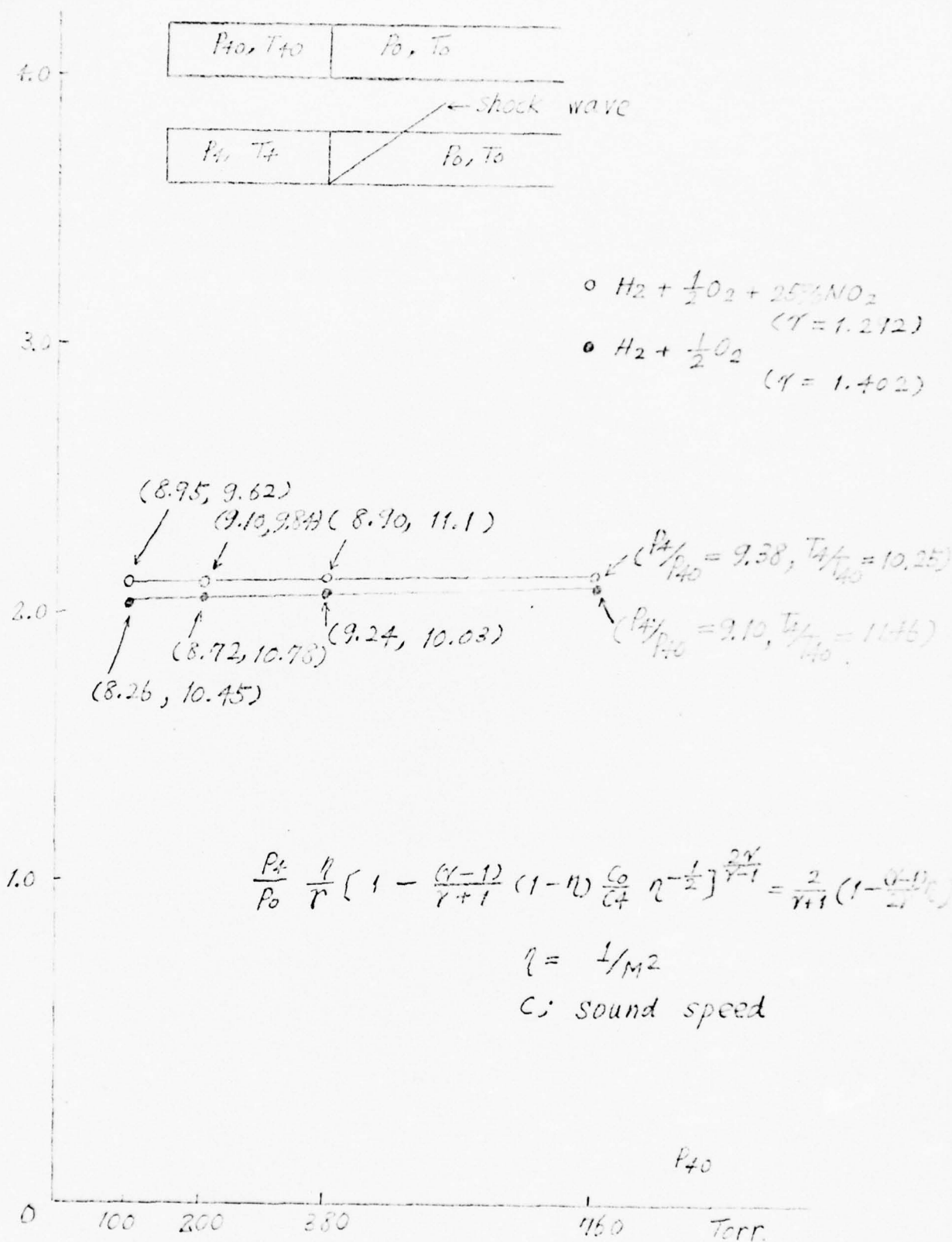
FIG·9 SHOCK STRENGTH FROM CONSTANT
VOLUME COMBUSTION DRIVER
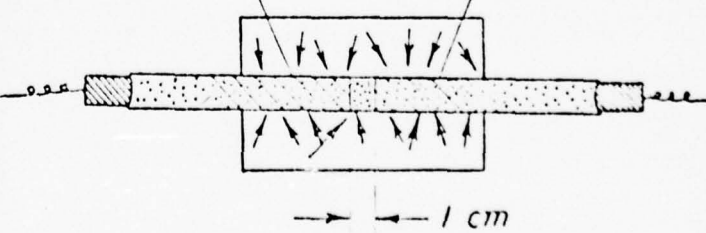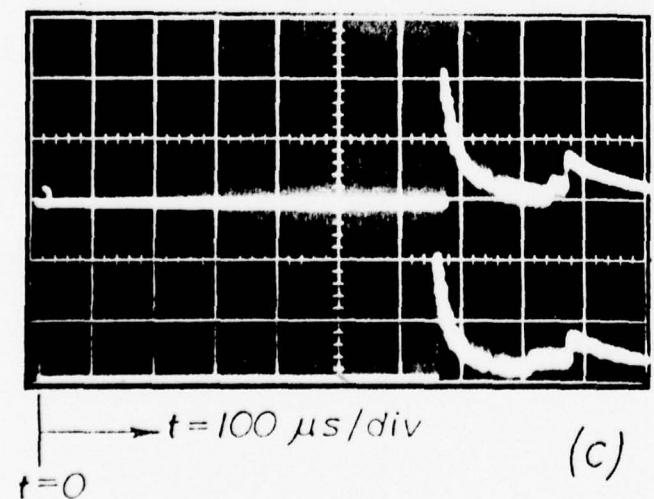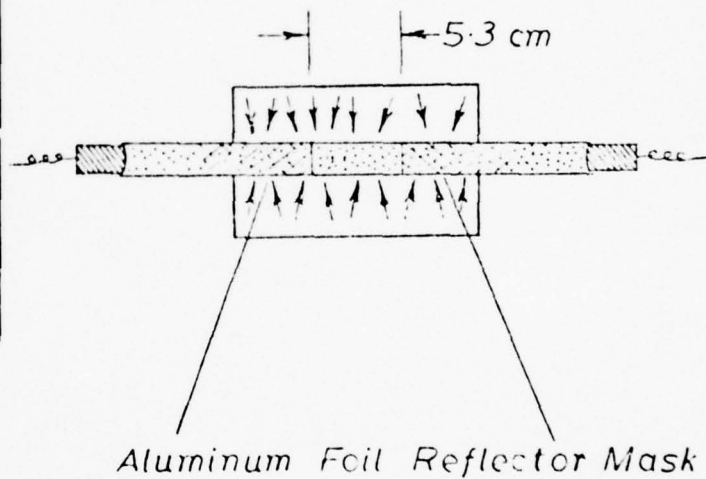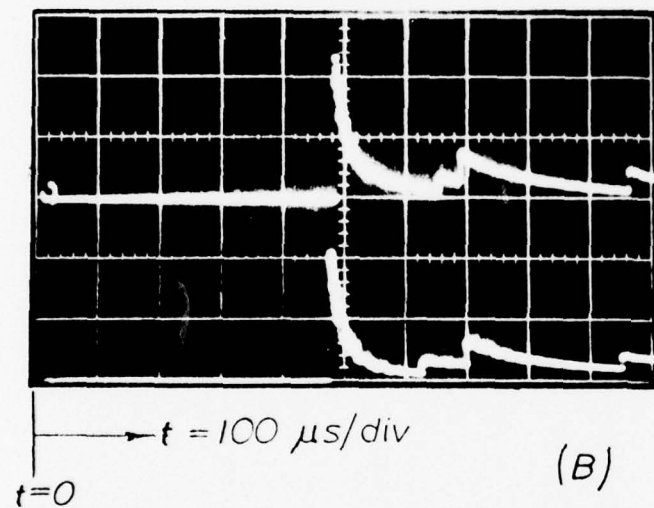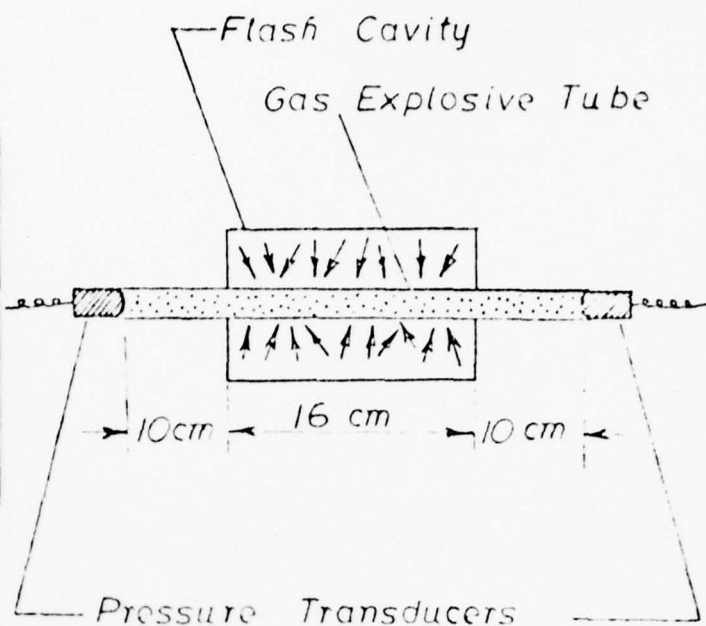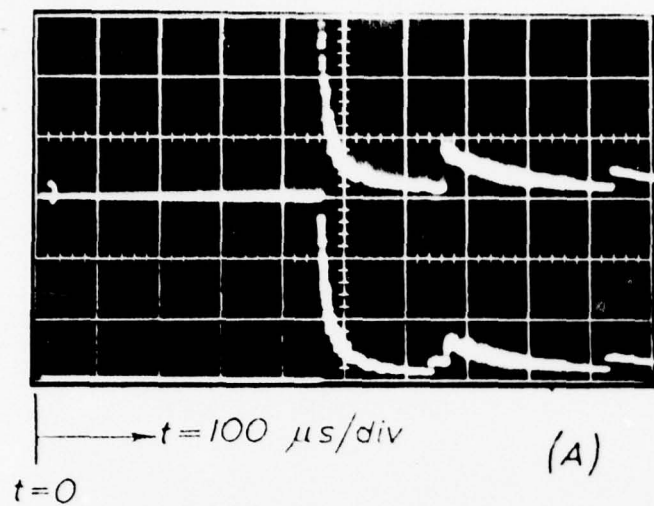
FIG. 10 Increase in Induction Time Due to Progressive
Masking of the Irradiated Volume

Flash Cavity

Gas Explosive Tube

16 cm

Blanking Plug

Pressure Transducer

$t_i = 440 \ \mu s$

(A)

$t_i = 750 \ \mu s$

9.7 cm

(B)

$t_i = 900 \ \mu s$

4 cm
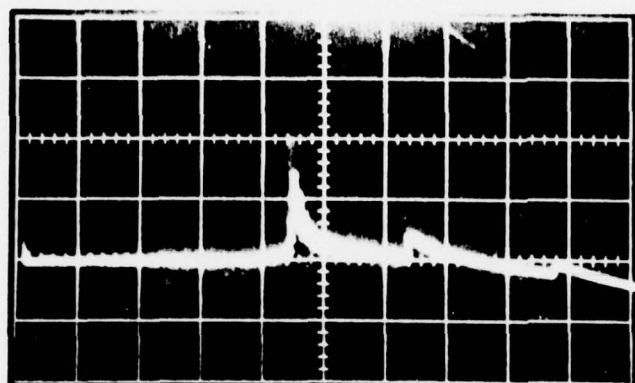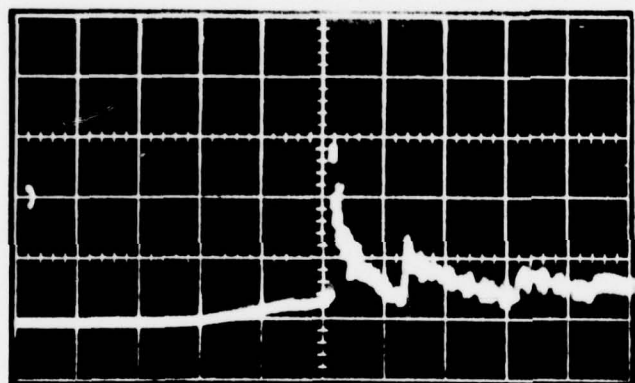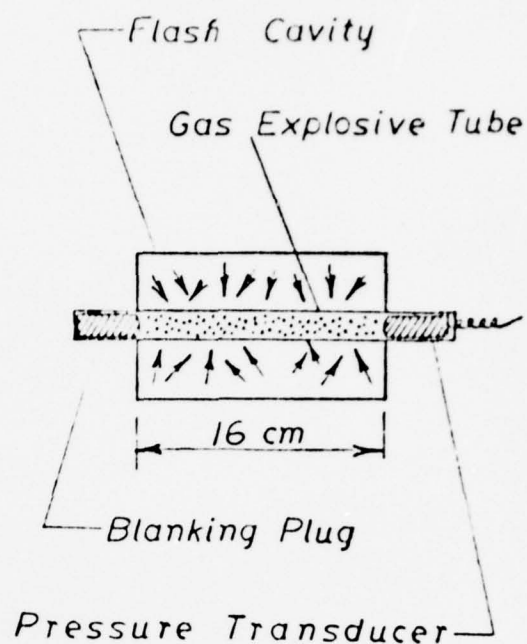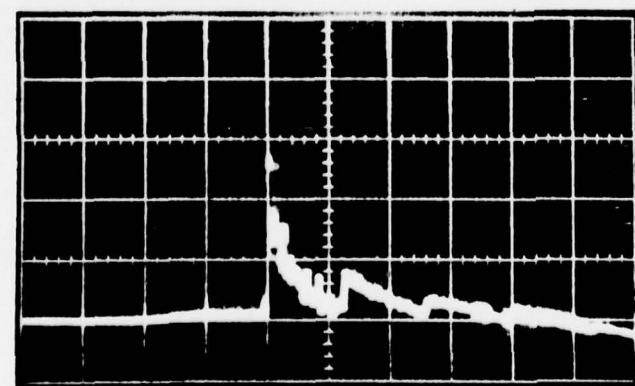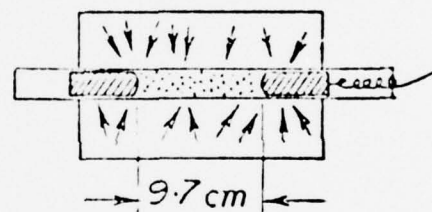
(C)
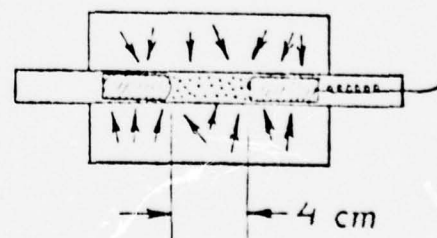
FIG. 11 Variation of Induction Time with Size of Irradiated Volume
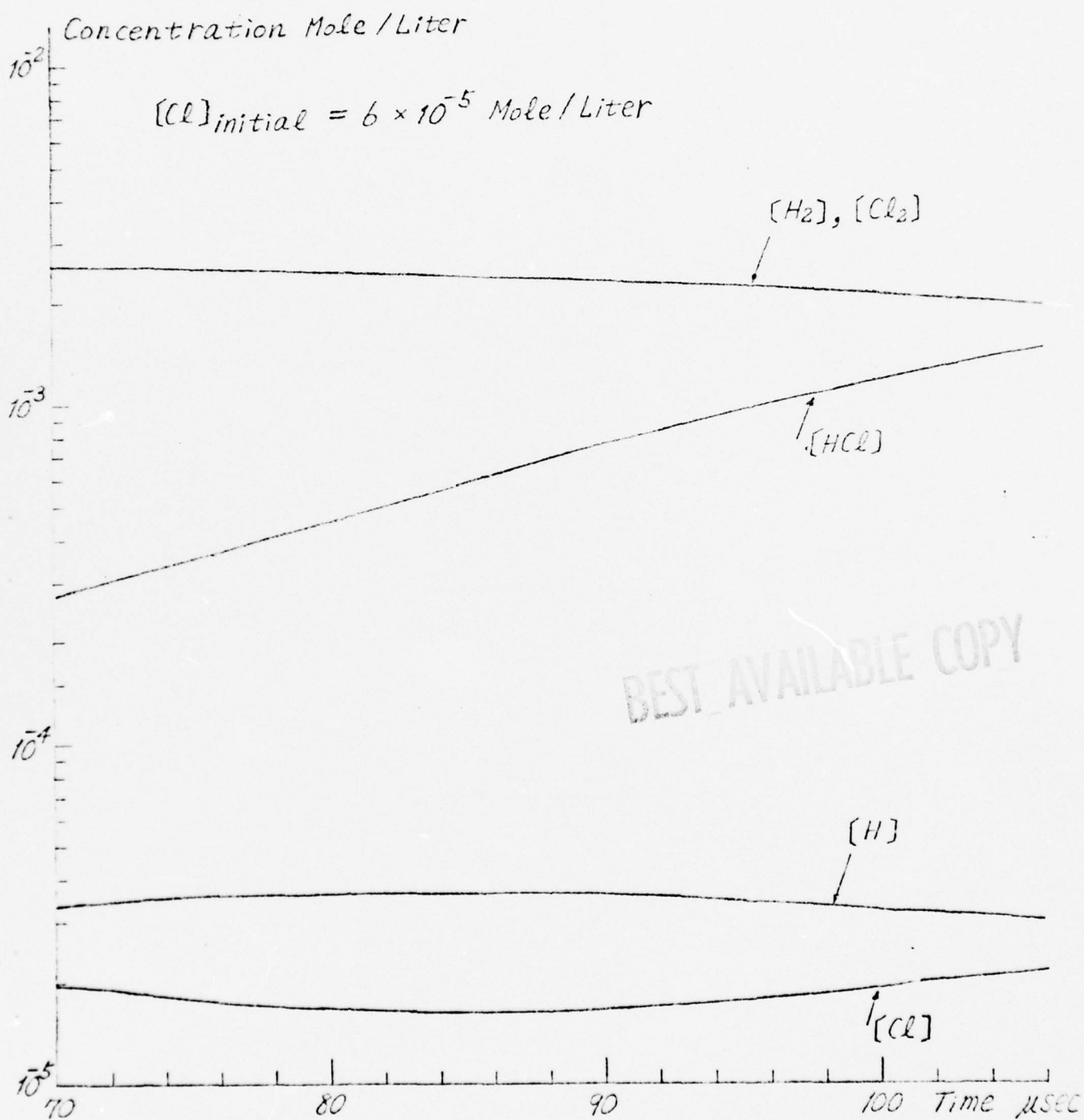
FIG·12 PRODUCTION OF SPECIES BY PHOTOCHEMICAL INITIATION
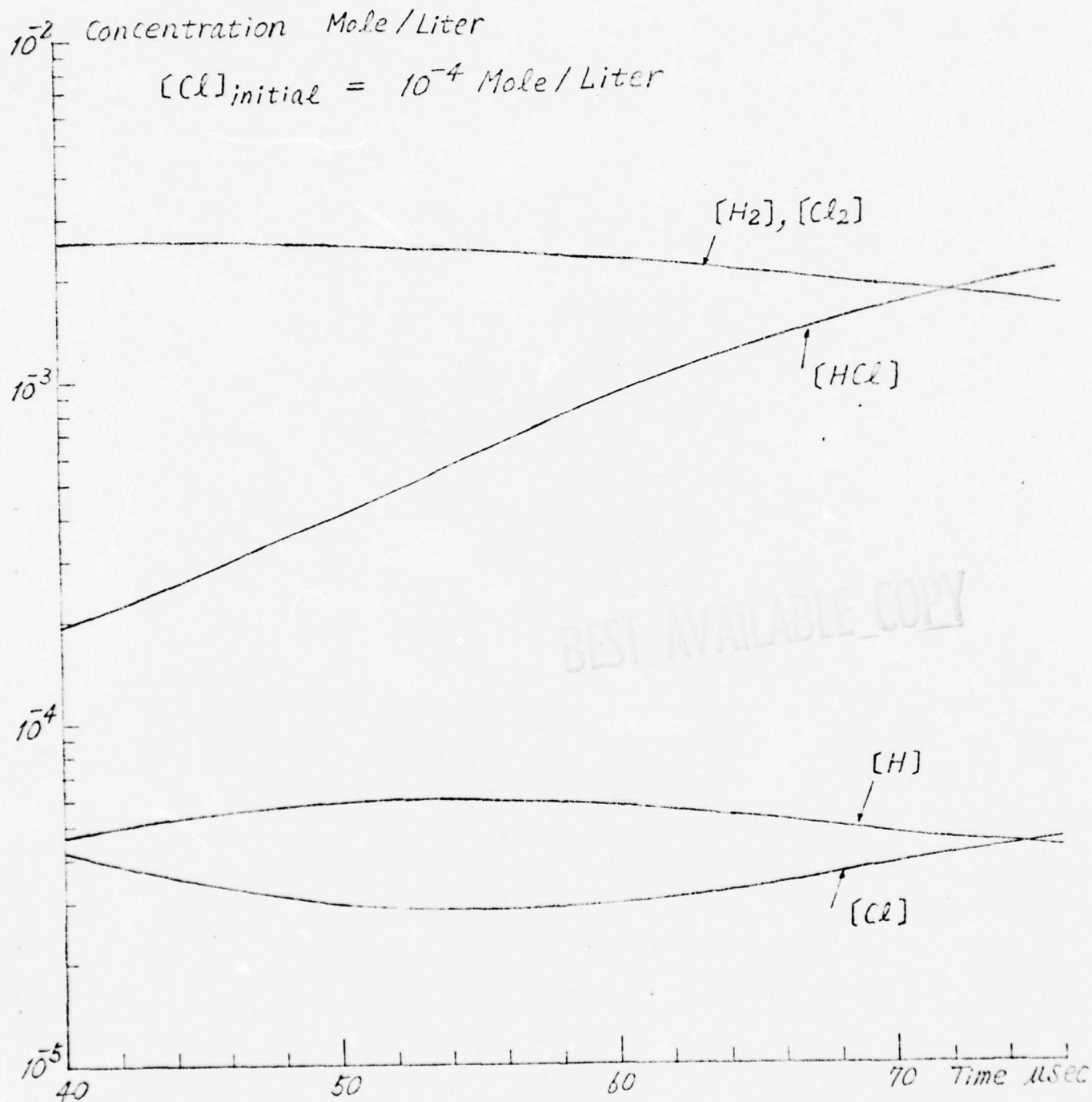
$H_2 + Cl_2$ 100 Torr, 298°K

FIG. 13   PRODUCTION OF SPECIES BY PHOTOCHEMICAL INITIATION

FIG·14 PRODUCTION OF SPECIES BY PHOTOCHEMICAL INITIATION

Concentration Mole / Liter $H_2 + Cl_2$ 100 Torr, 298°K

$[Cl]_{initial} = 5 \times 10^{-4}$ Mole / Liter

[H_2]

[Cl_2]

[HCl]

[Cl_2]

[H_2]

[Cl]

[H]

10^{-3}

10^{-4}

10^{-5}

10^{-6}

0   5   10   15   Time μsec
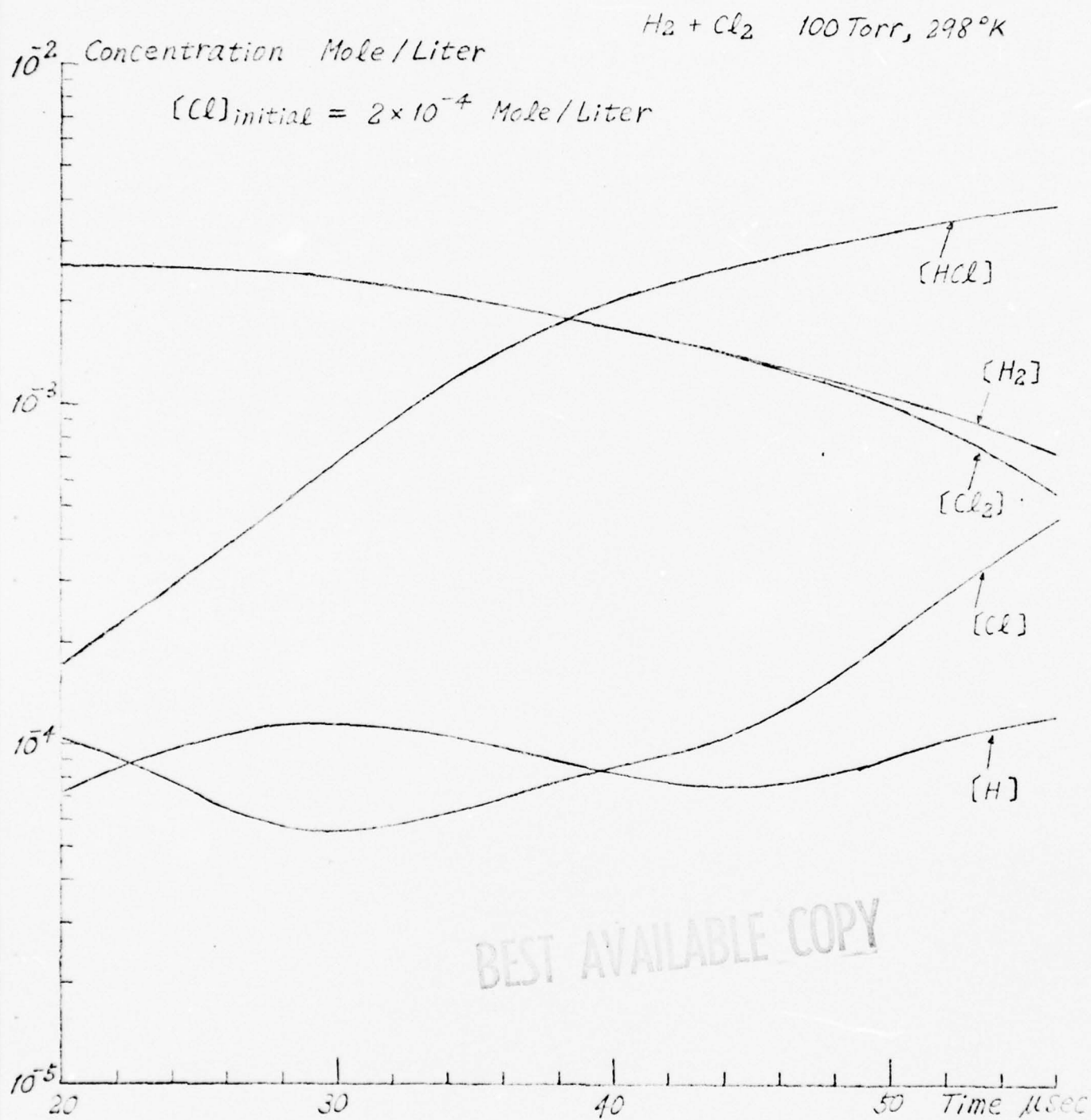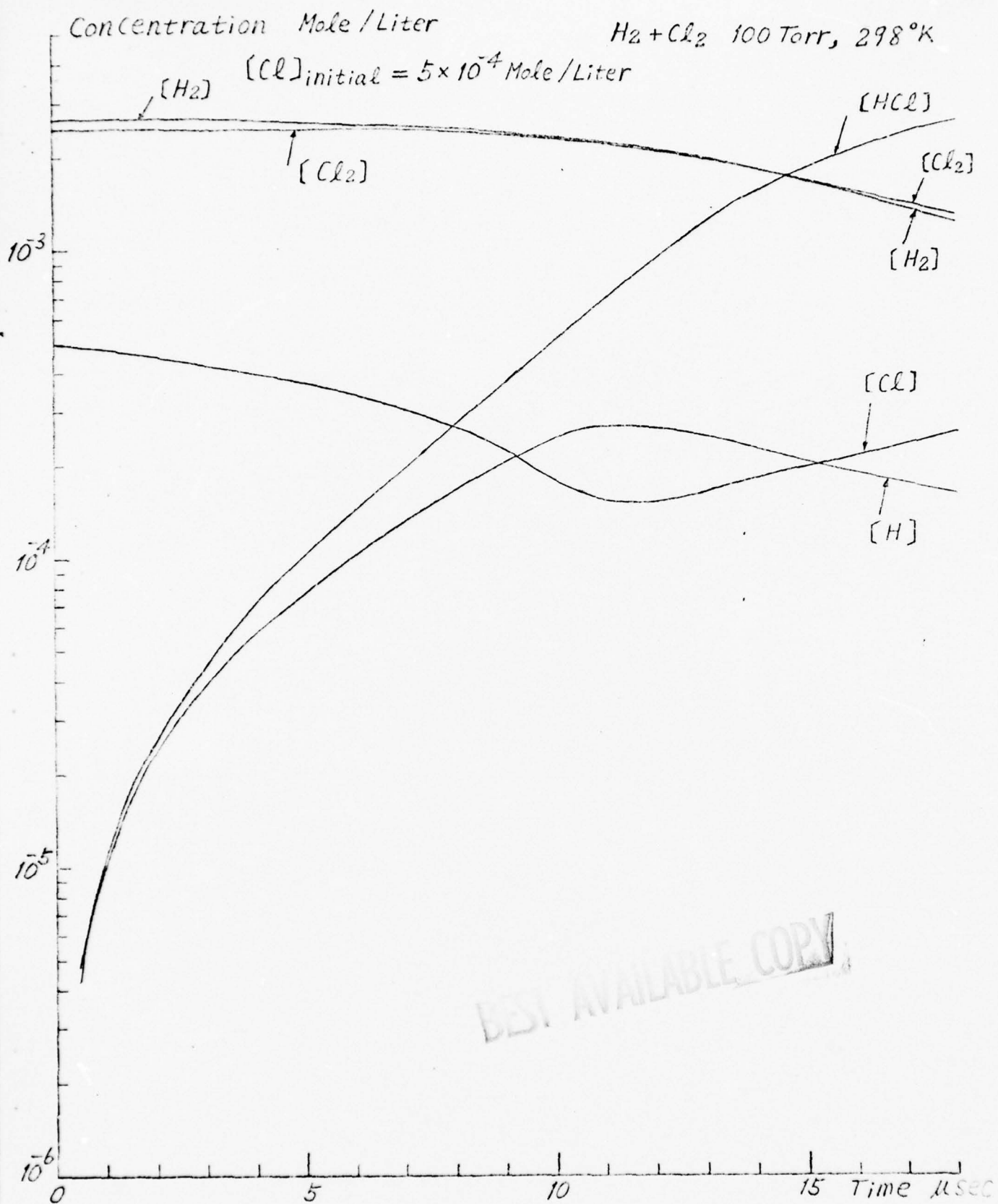
FIG·15   PRODUCTION OF SPECIES BY PHOTOCHEMICAL
INITIATION

FIG. 16 PRODUCTION OF SPECIES BY PHOTOCHEMICAL
INITIATION

$H_2 + Cl_2$ 100 Torr, 298°K

Concentration Mole/Liter

$[Cl]_{initial} = 2.5 \times 10^{-3}$ Mole / Liter

$[HCl]$

$[Cl]$

$[H_2]$

$[H]$

$[Cl_2]$

Time μsec
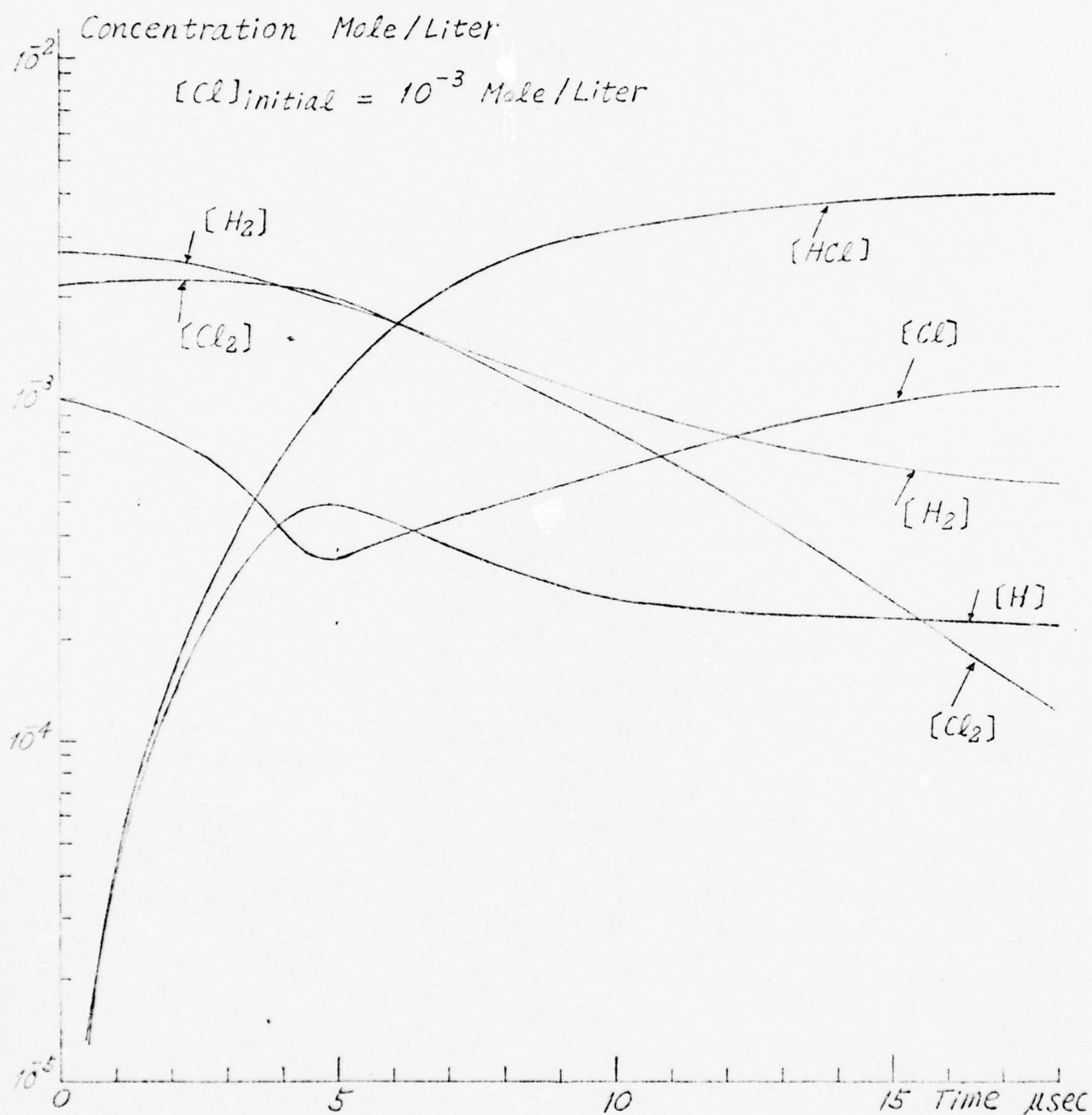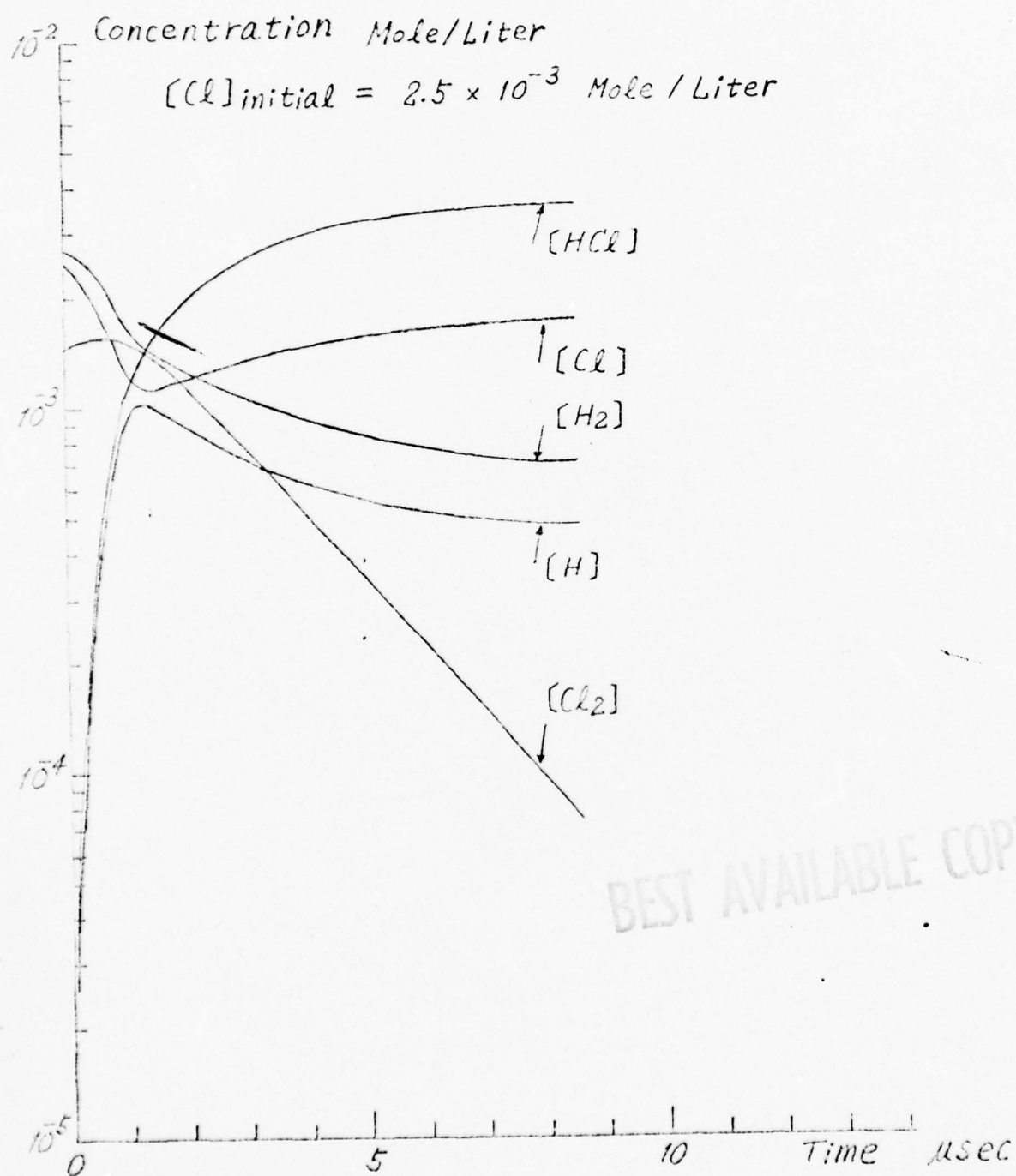
FIG·17 PRODUCTION OF SPECIES BY PHOTOCHEMICAL
INITIATION
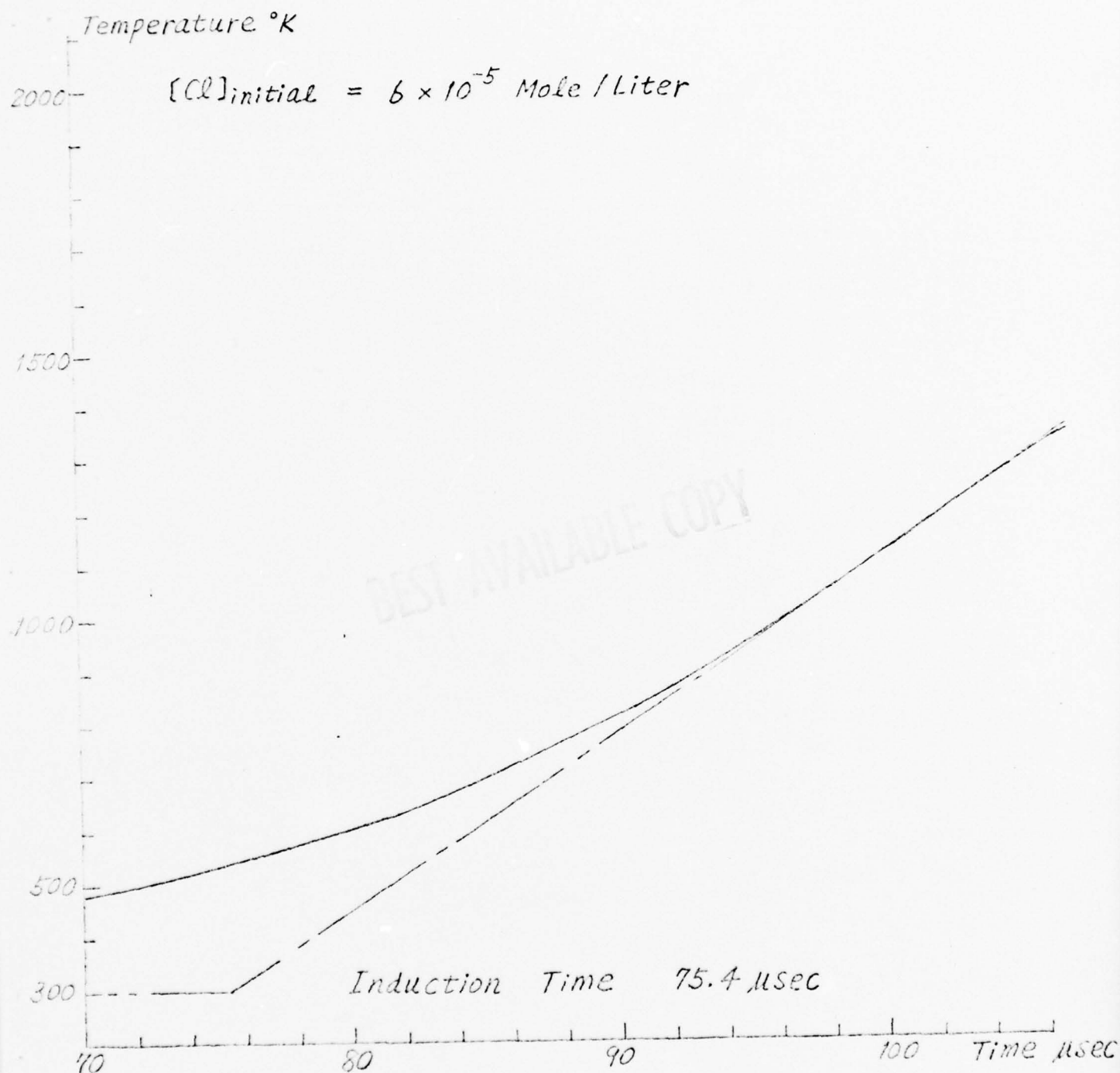
FIG·18 TEMPERATURE-TIME PROFILES FOR PHOTOCHEMICAL
INITIATION
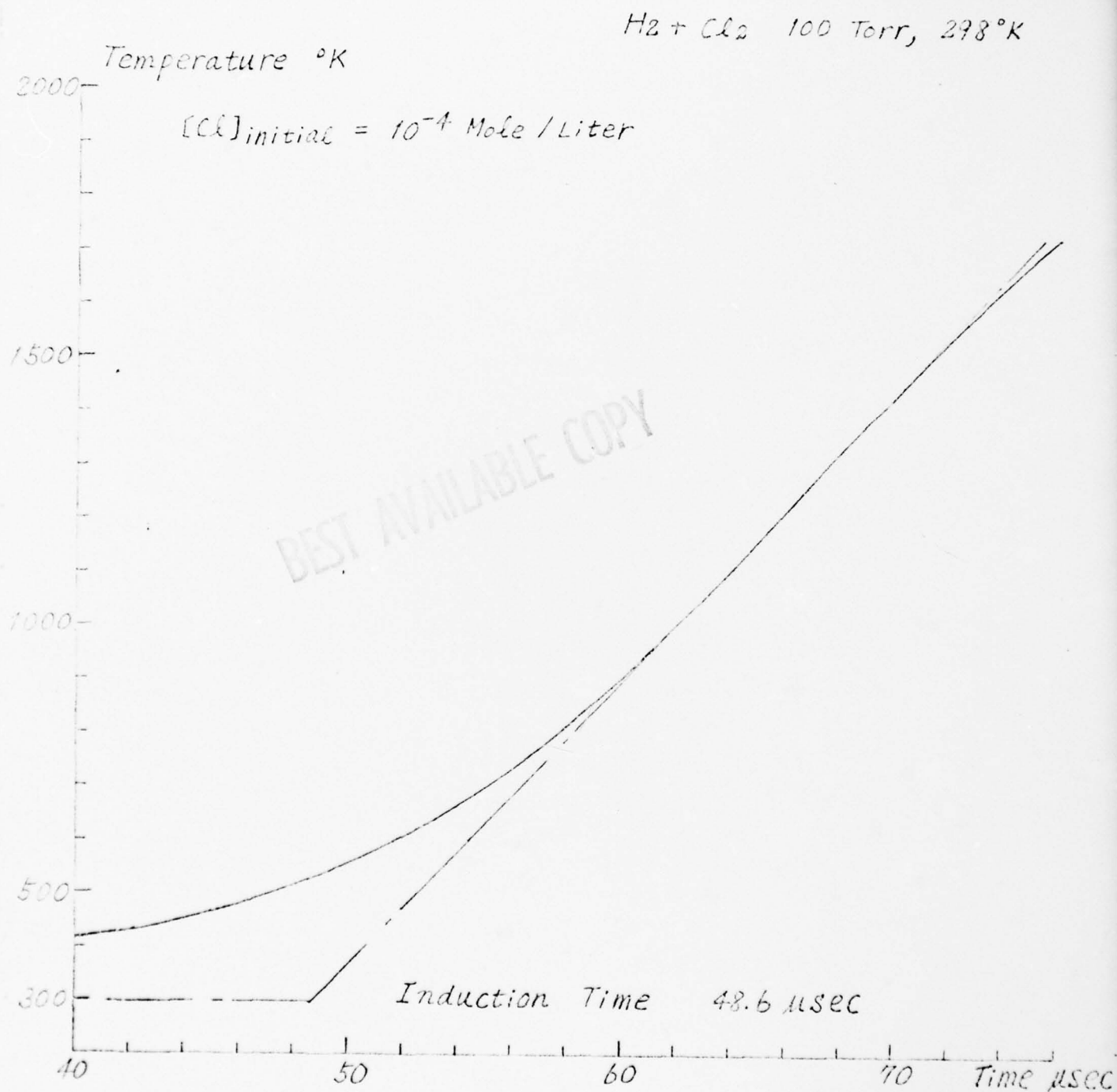
FIG·19 TEMPERATURE-TIME PROFILES FOR PHOTOCHEMICAL INITIATION

FIG. 20 TEMPERATURE - TIME PROFILES FOR PHOTOCHEMICAL INITIATION

Temperature °K

$H_2 + Cl_2$ 100 Torr, 298°K

$[Cl]_{initial} = 2 \times 10^{-4}$ Mole / Liter

Induction Time   26.5 μsec

Time   μsec
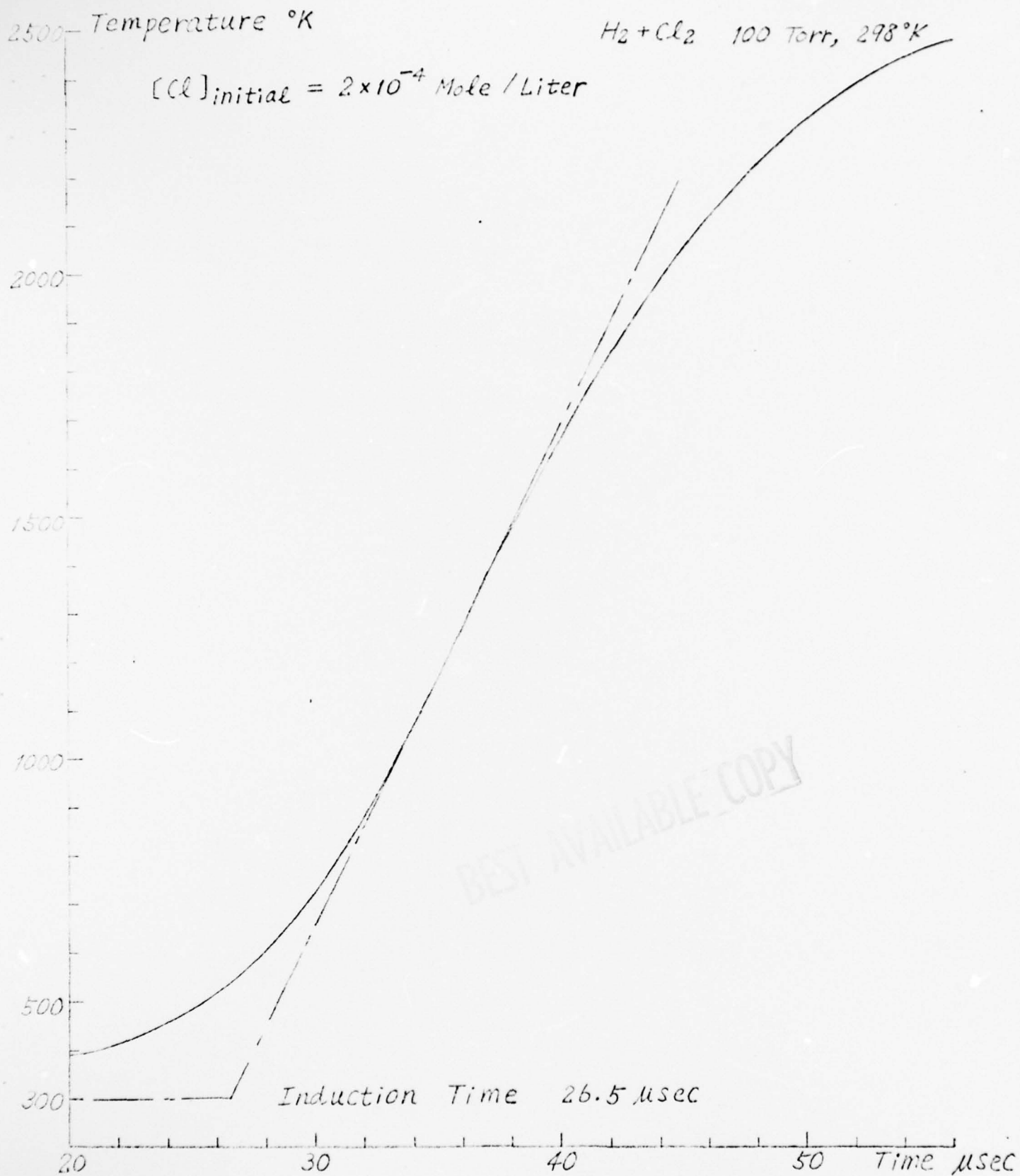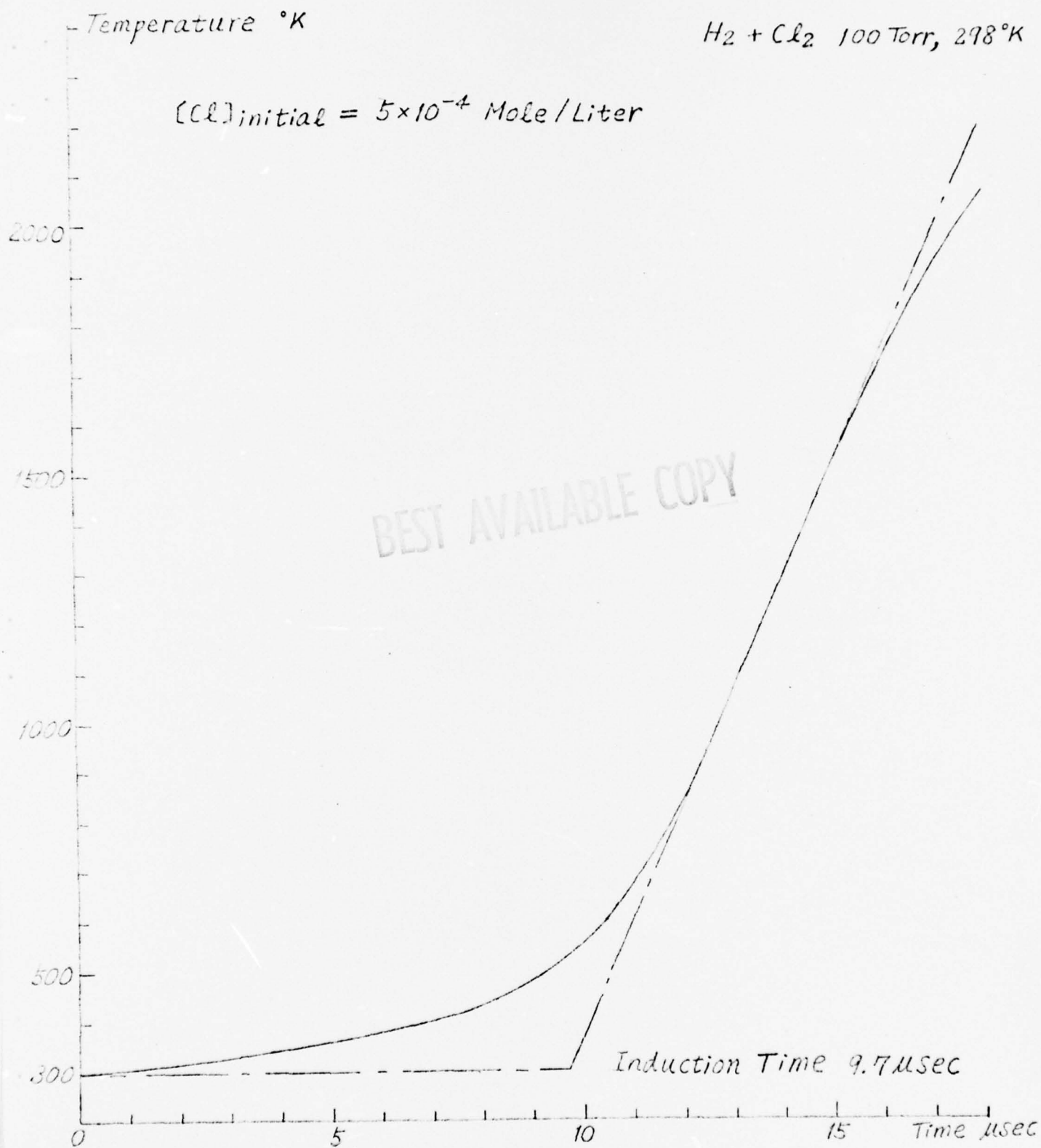
FIG·21 TEMPERATURE-TIME PROFILES FOR PHOTOCHEMICAL INITIATION
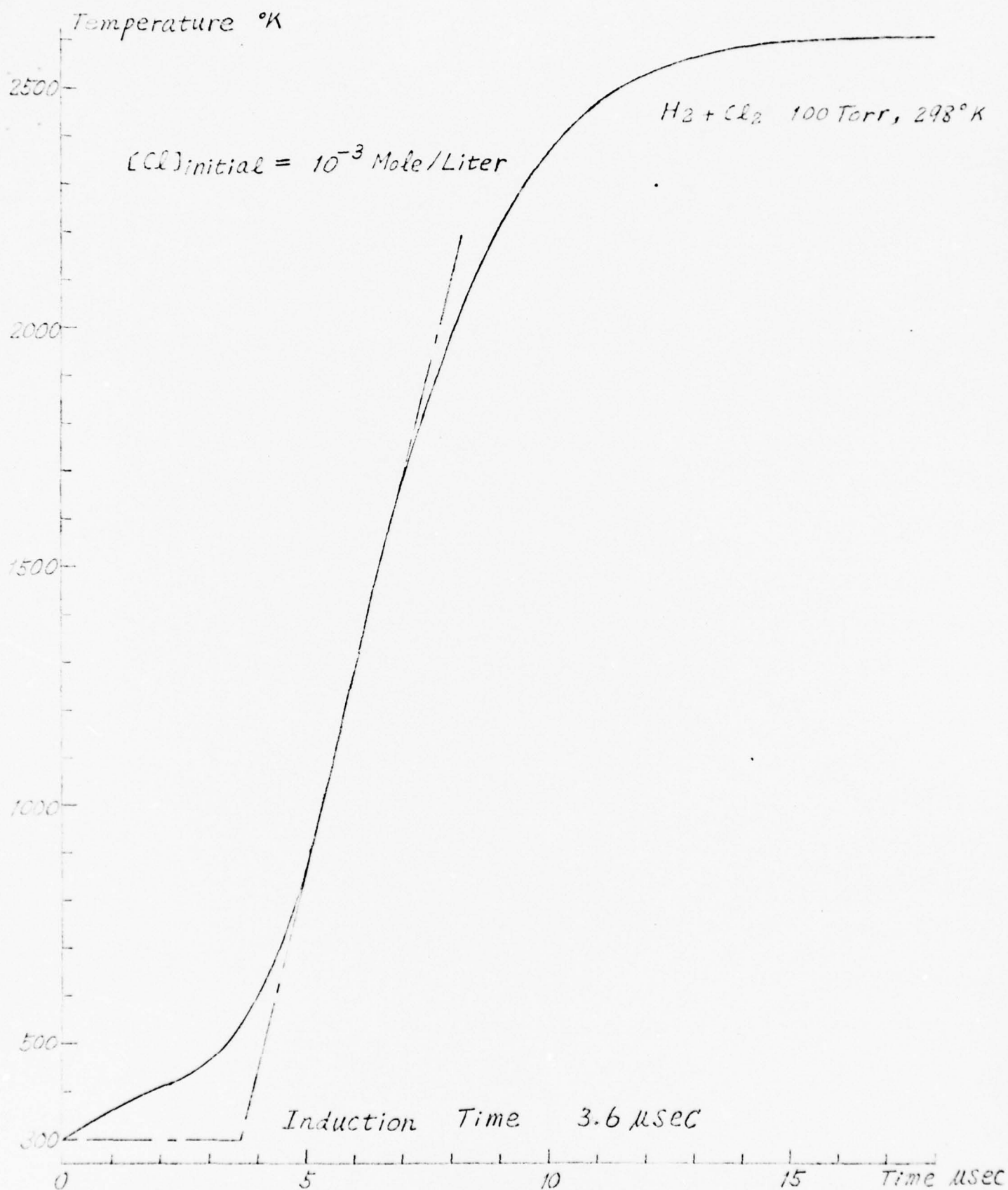
FIG·22 TEMPERATURE - TIME PROFILES FOR PHOTOCHEMICAL INITIATION

FIG·23 TEMPERATURE-TIME PROFILES FOR PHOTOCHEMICAL INITIATION
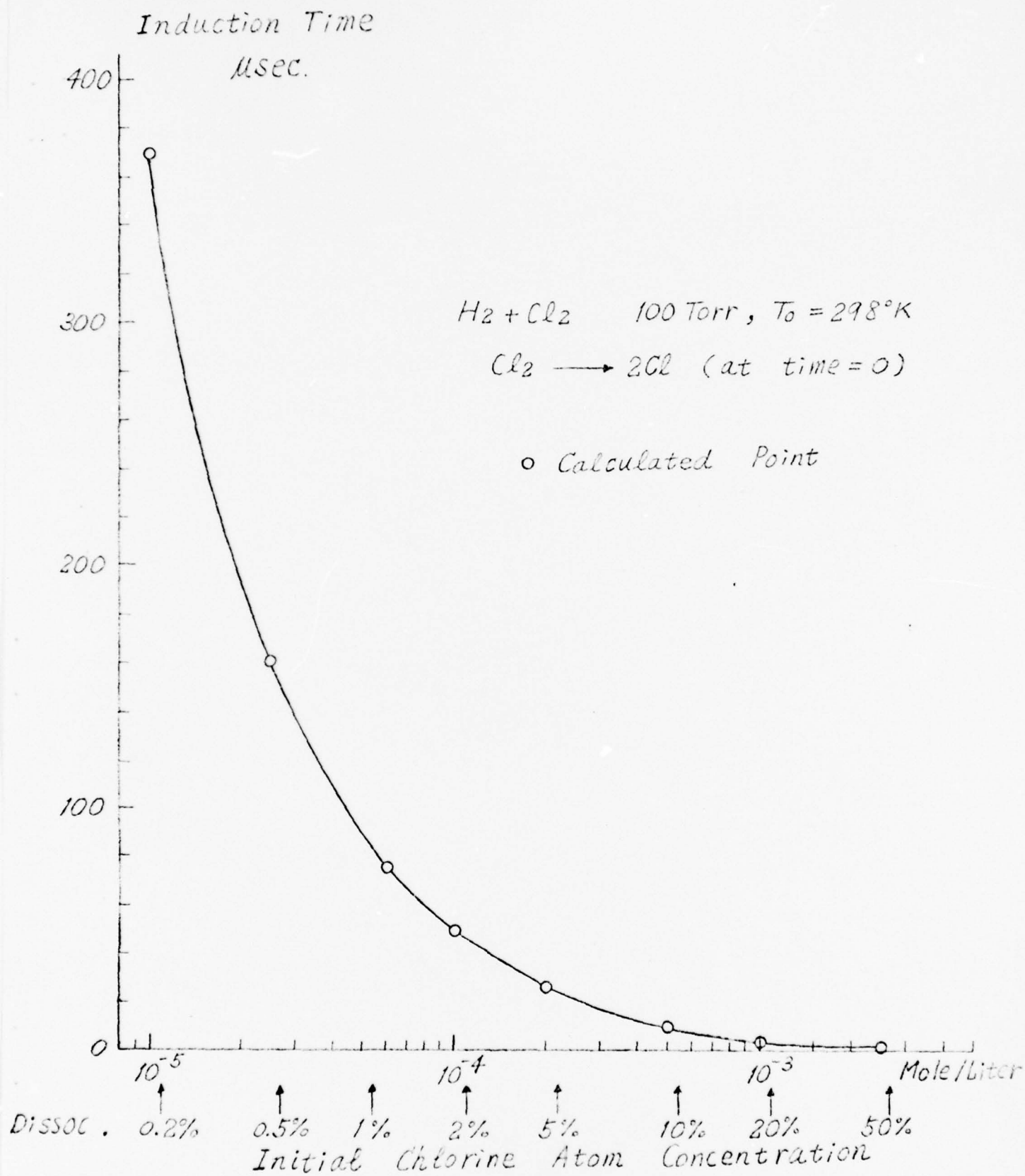
FIG·24 VARIATION OF INDUCTION TIME WITH INITIAL FREE RADICAL CONCENTRATION
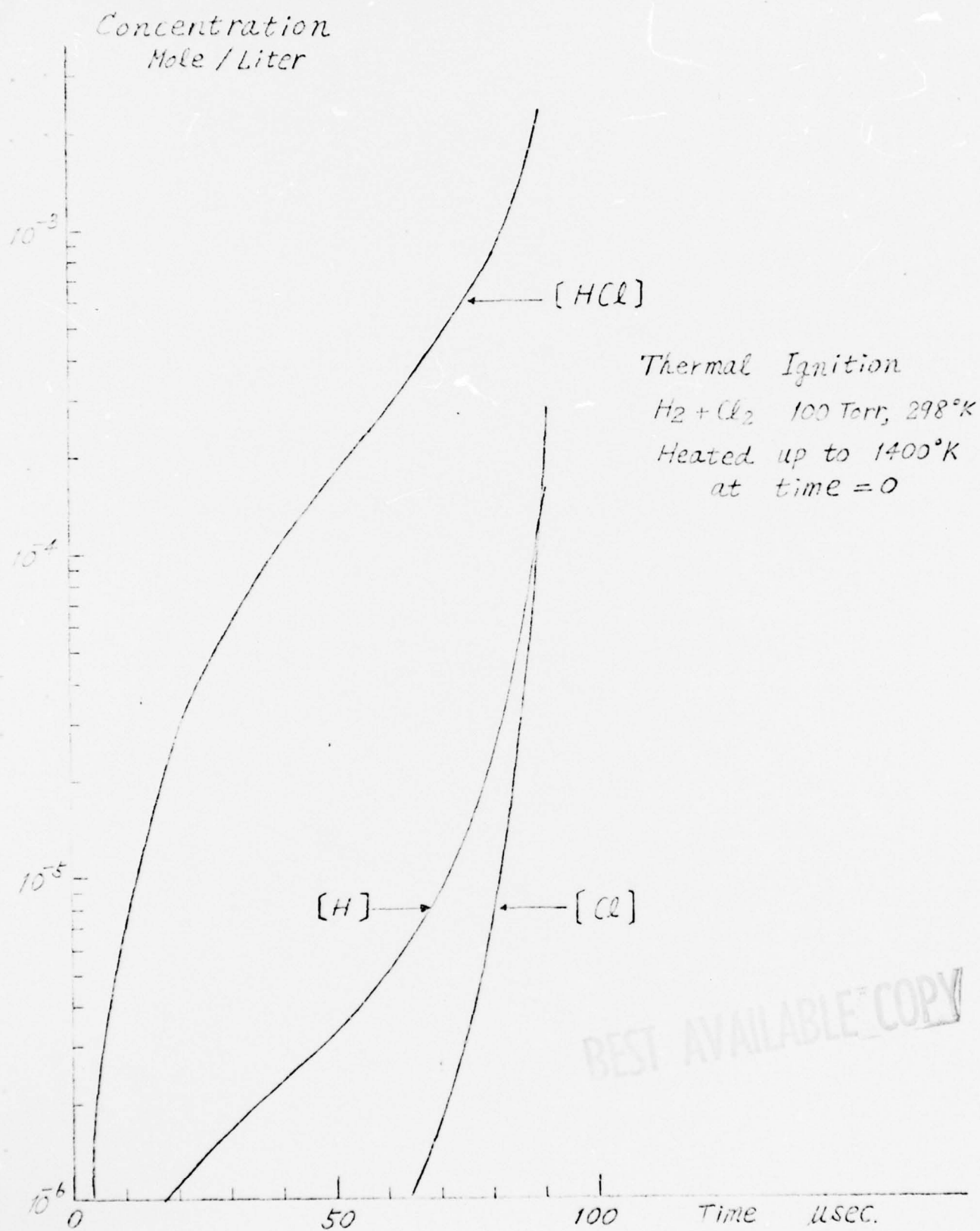
FIG·25 PRODUCTION OF SPECIES BY THERMAL INITIATION
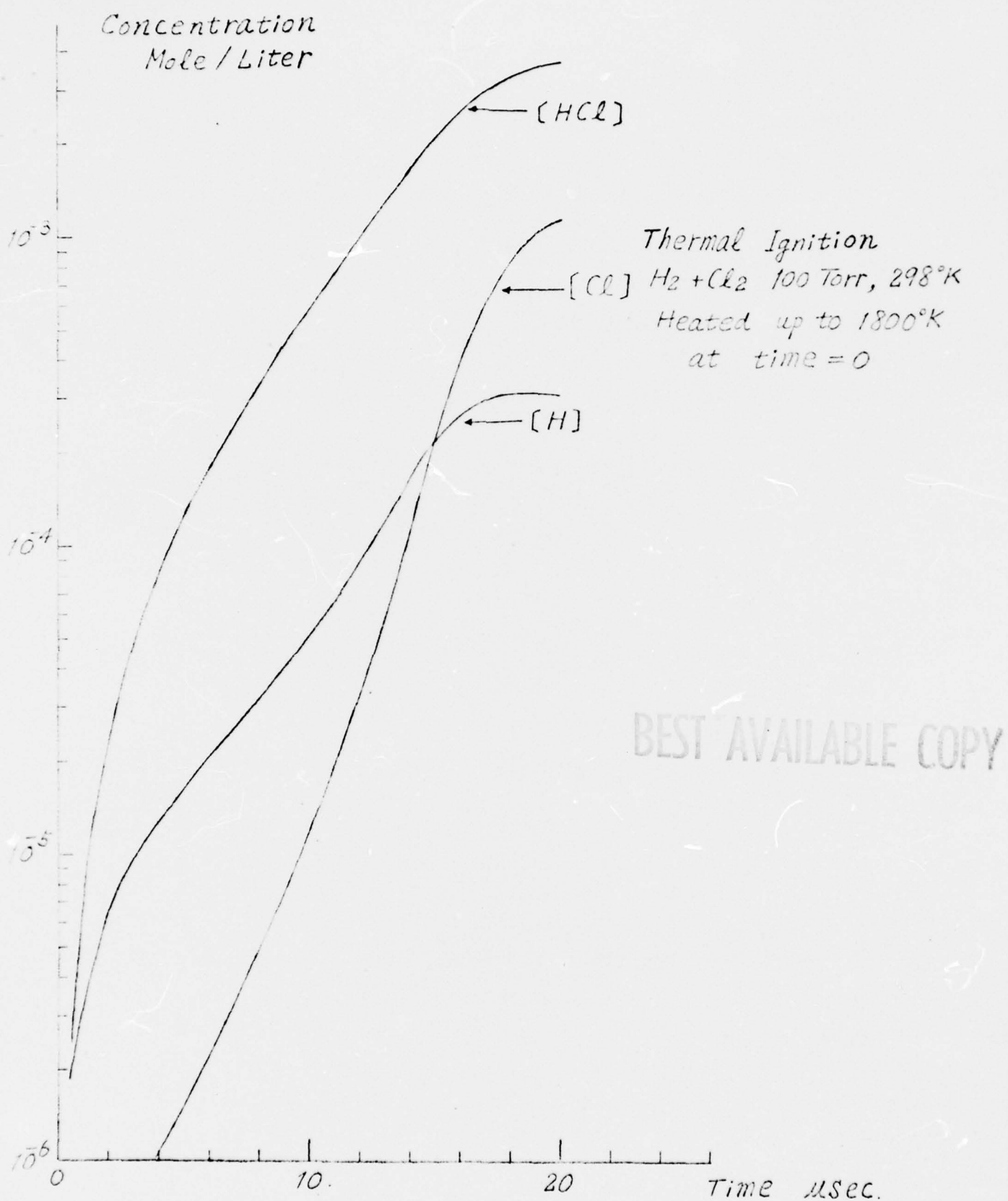
FIG·26 PRODUCTION OF SPECIES BY THERMAL INITIATION

Thermal Ignition
$H_2 + Cl_2$ 100 Torr, 298°K
Heated up to 1400°K
at time = 0

$\left.\dfrac{dT}{dt}\right)_{MAX} = 8.9 \times 10^{1}$ °K / µsec

Induction Time 78 µsec

FIG·27 TEMPERATURE-TIME PROFILES FOR THERMAL INITIATION

Temperature °K

3000

Thermal Ignition
$H_2 + Cl_2$ 100 Torr, 298°K
Heated up to 1800°K
at time = 0

2500

2000

$$\frac{dT}{dt}\Big)_{MAX} = 2.5 \times 10^2 \; °K / \mu sec$$

Induction Time 9.2 μsec.

1500

0   10   20   Time μsec
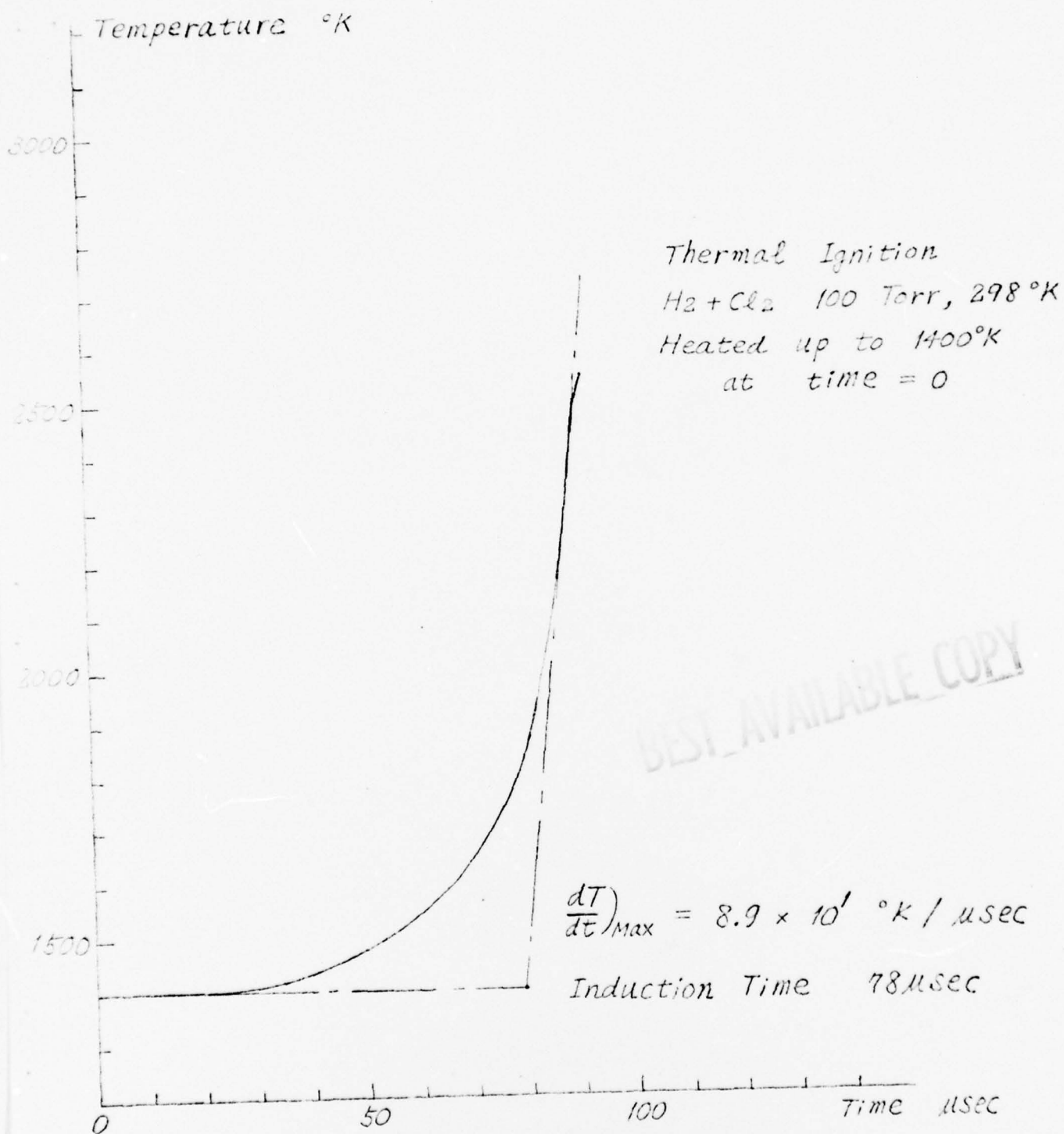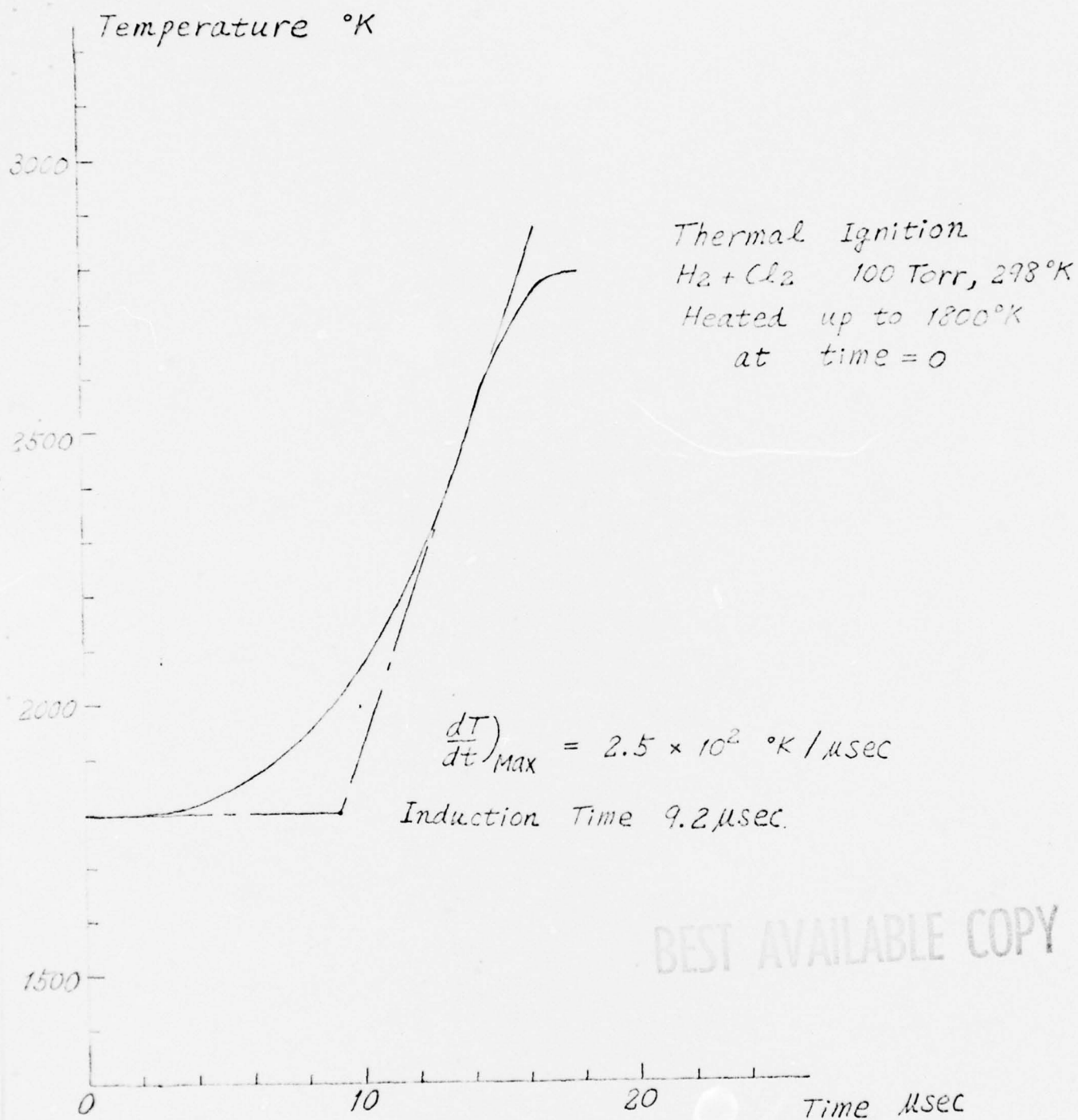
FIG·28 TEMPERATURE-TIME PROFILES FOR THERMAL INITIATION
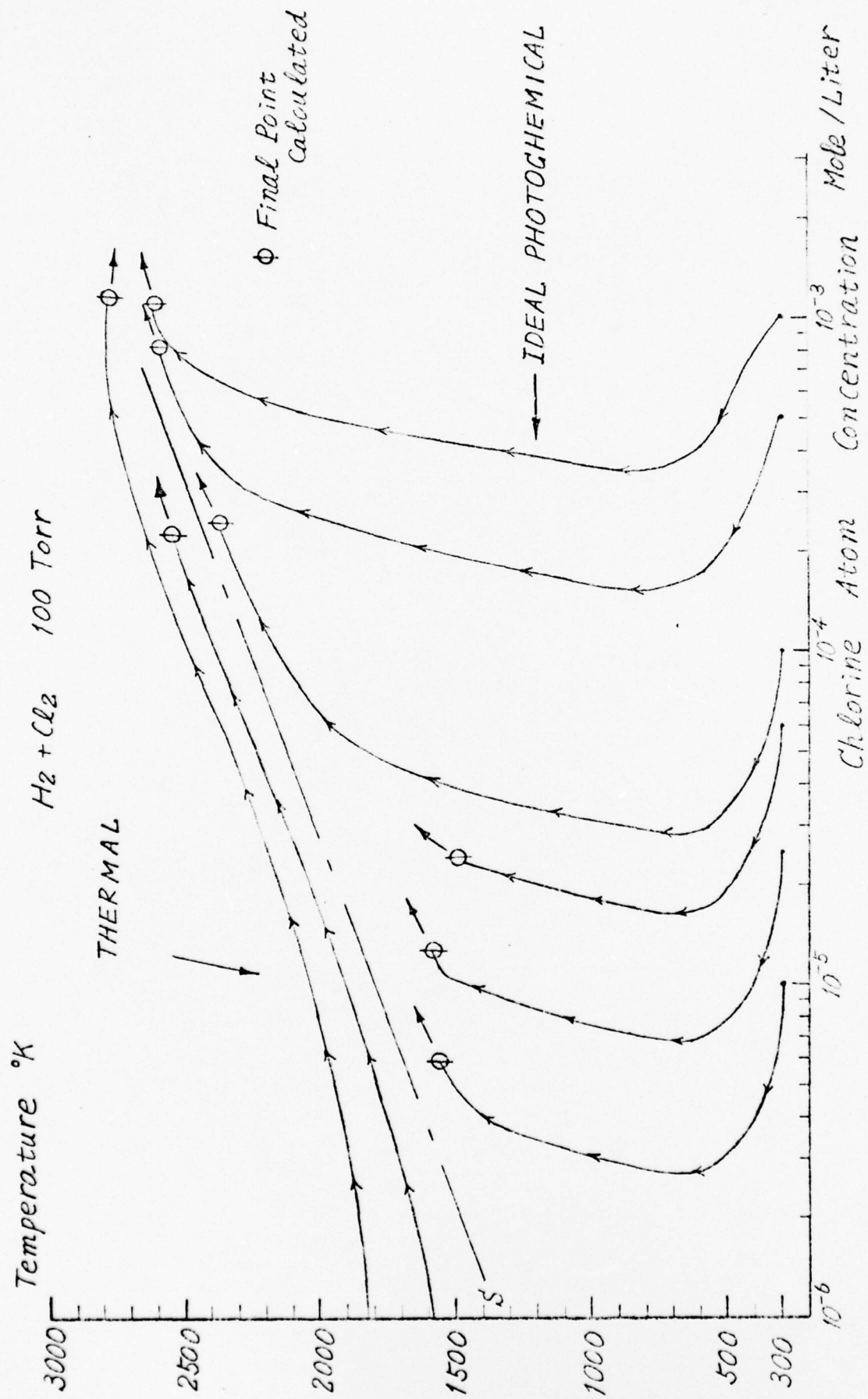
FIG. 29 PHASE DIAGRAM DISTINGUISHING BETWEEN THERMAL
AND PHOTOCHEMICAL IGNITION
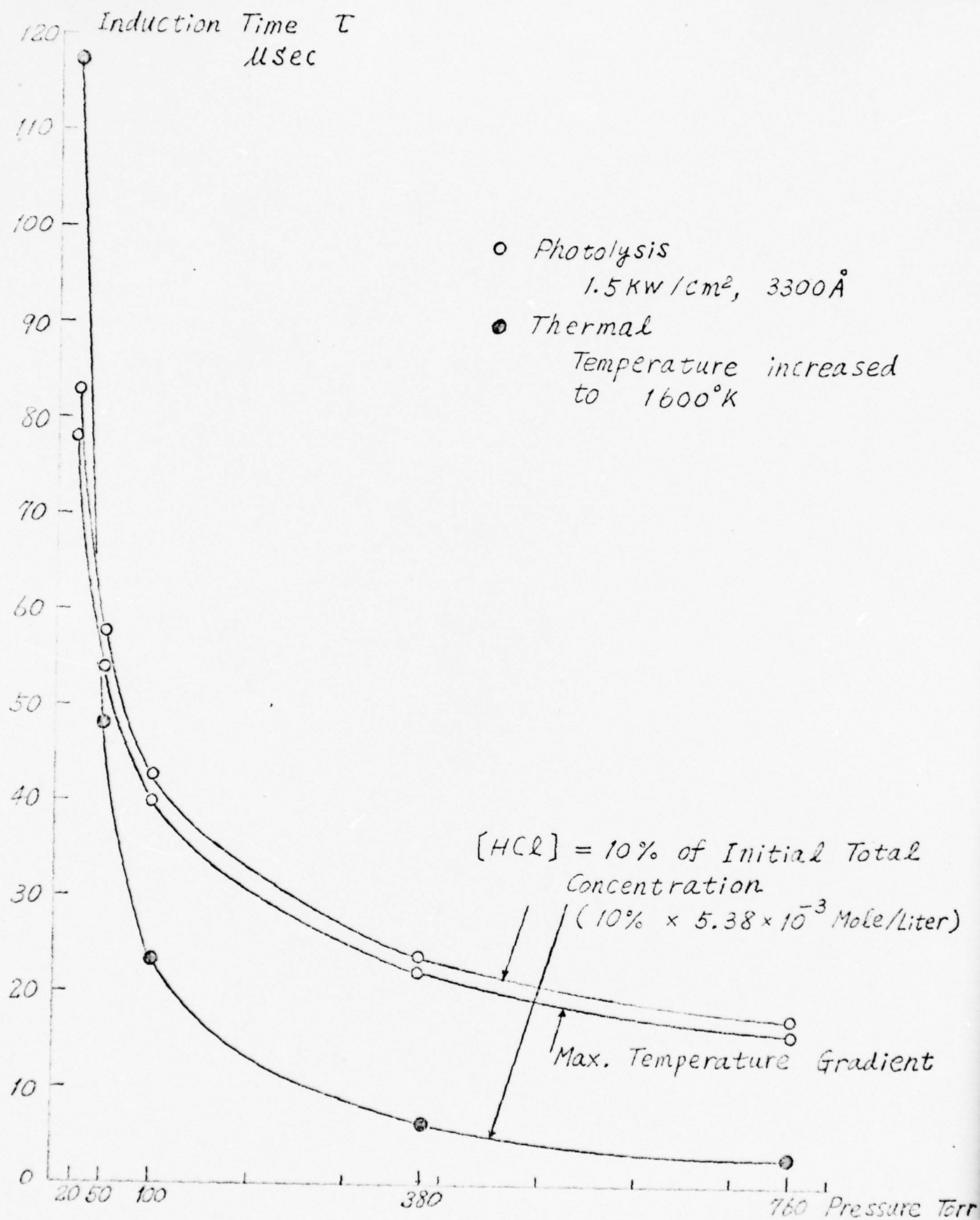
FIG.30 VARIATION OF INDUCTION TIME WITH INITIAL PRESSURE
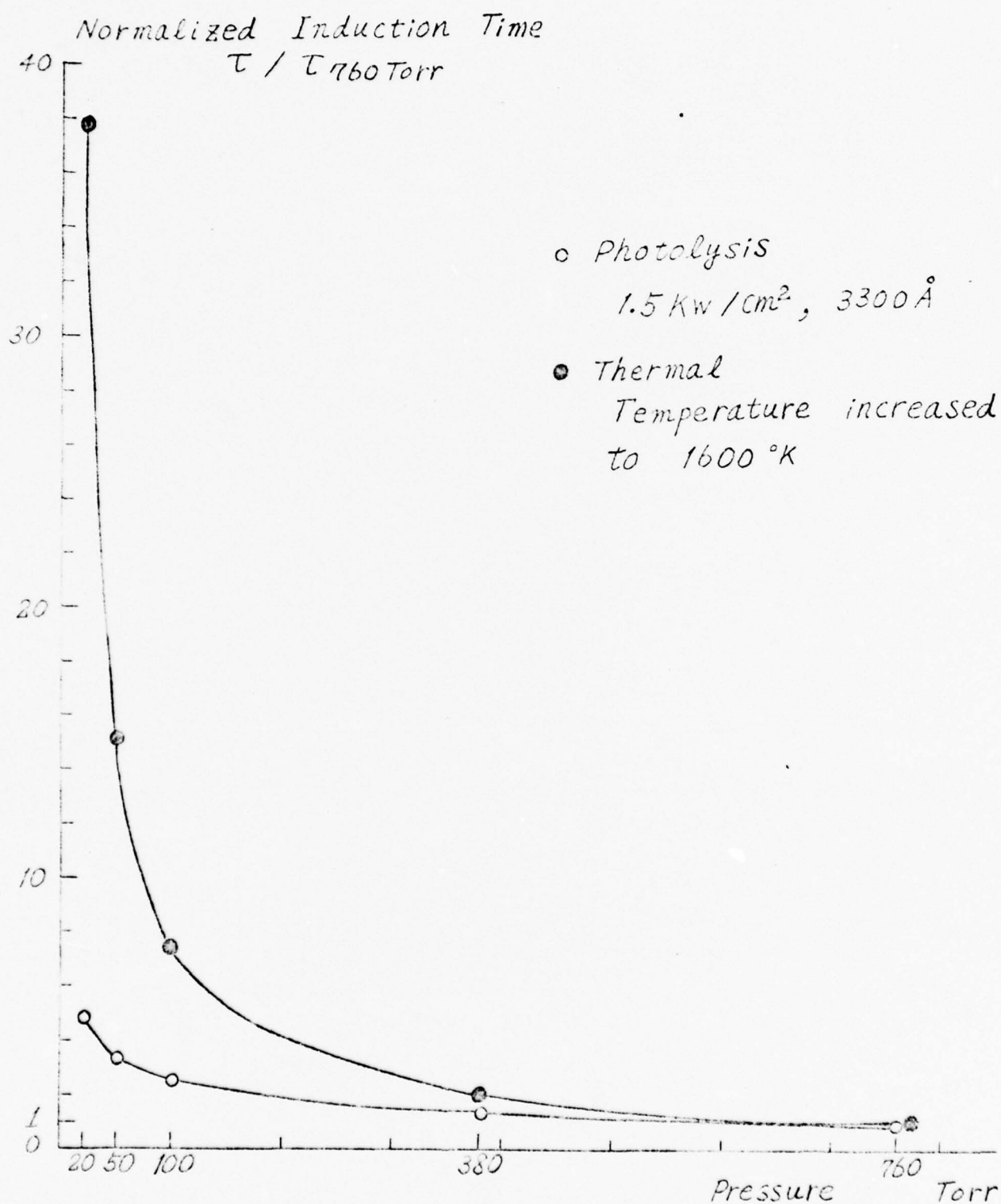
FIG·31   RELATIVE EFFICIENCY OF THERMAL AND
PHOTOCHEMICAL INITIATION

SCHLIEREN PHOTOGRAPHY

FLASH TUBE

QUARTZ WINDOWS
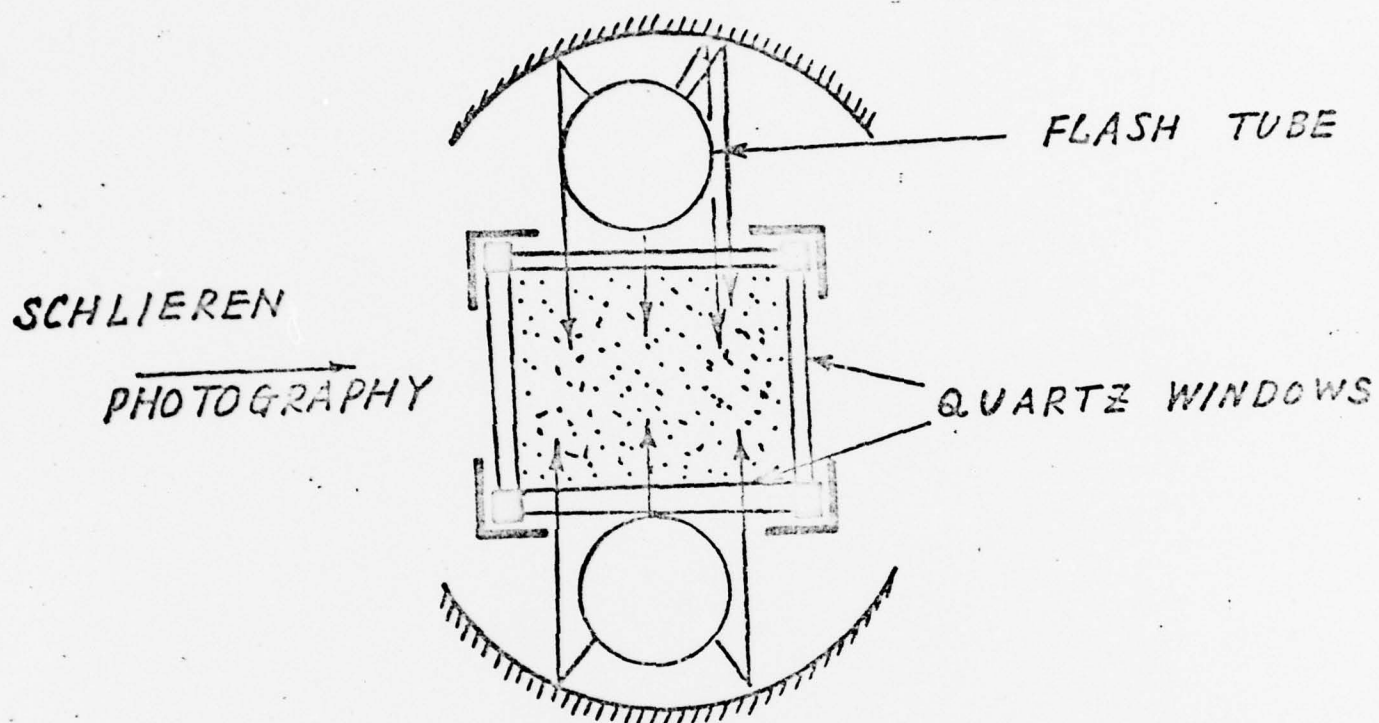
FIG. 32   PHOTOCHEMICAL INITIATION OF DETONATION
IN THE RECTANGULAR EXPLOSION CHAMBER
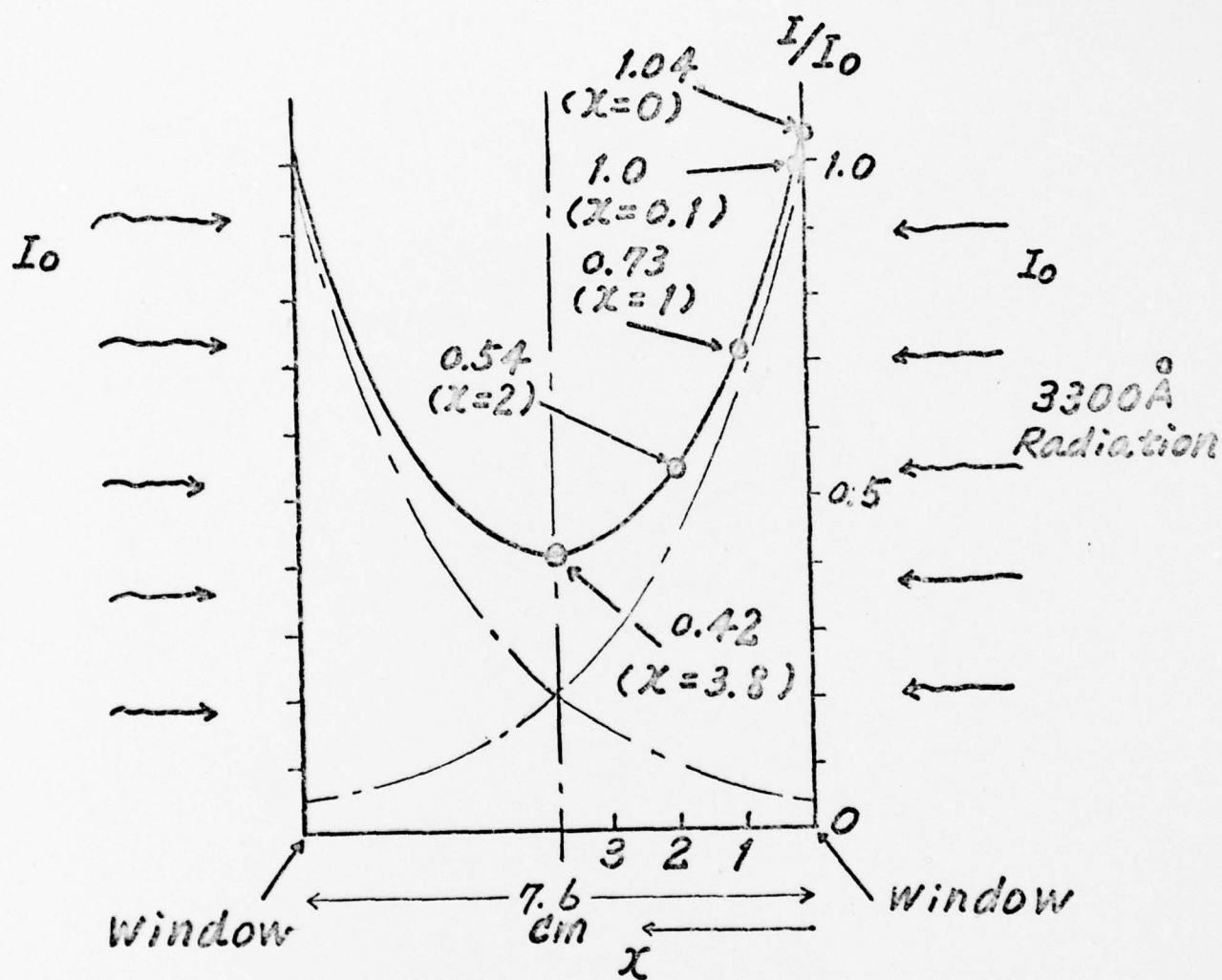
FIG·33   ABSORPSION OF UV RADIATION BY CHLORINE GAS
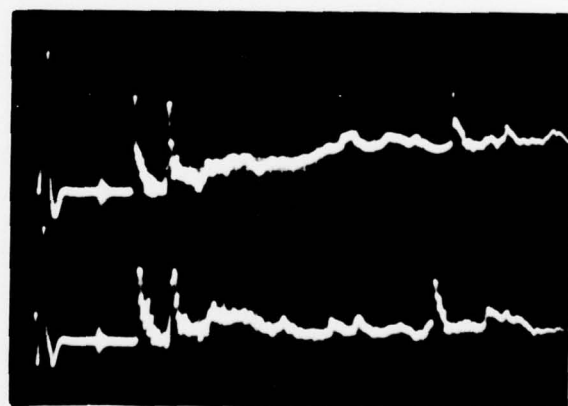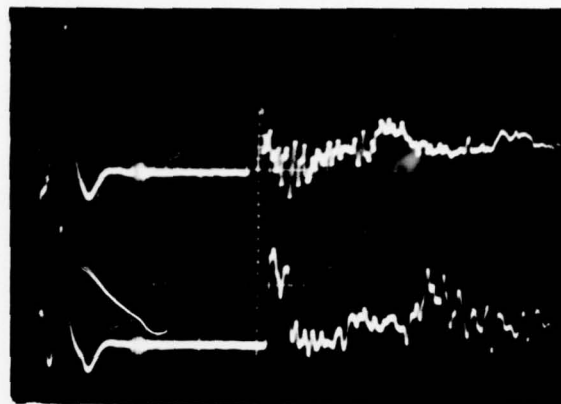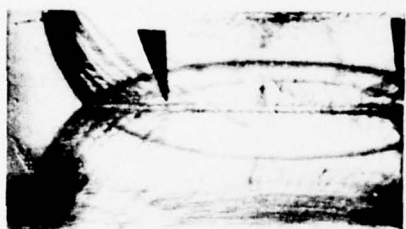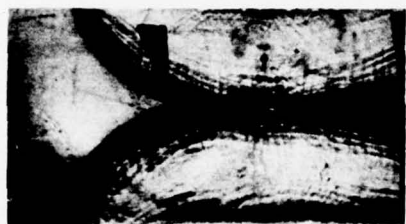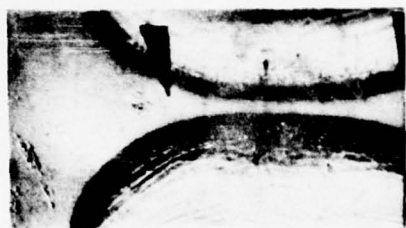
FIG· 34 MACH COLLISION OF COMBUSTION WAVES
INITIATED PHOTOCHEMICALLY
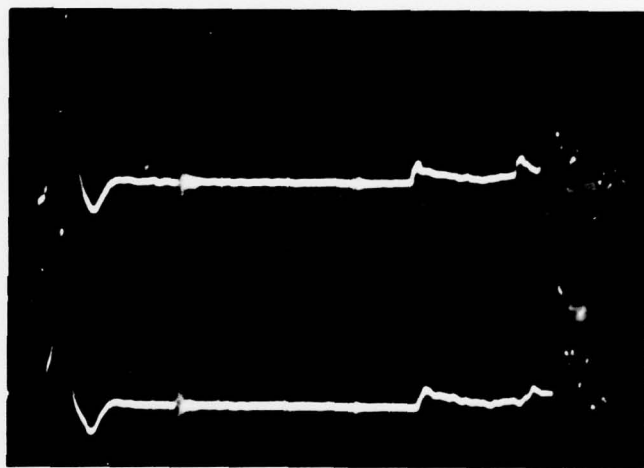
FIG·35 PHOTOCHEMICAL INITIATION OF DEFLAGRATION
IN EQUIMOLAR $H_2 - Cl_2$ MIXTURE AT 100 TORR
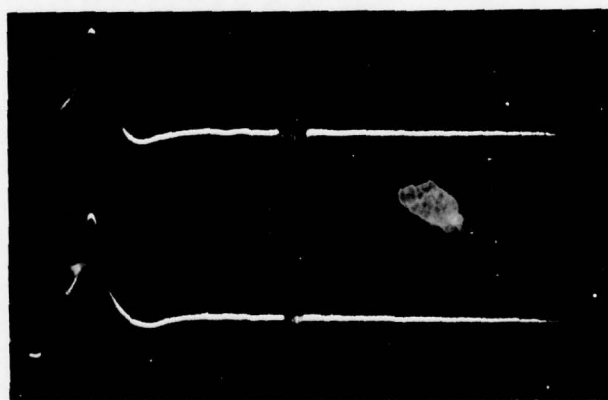
FIG. 36   UV   PHOTOIRRADIATION   OF   CHLORINE   GAS
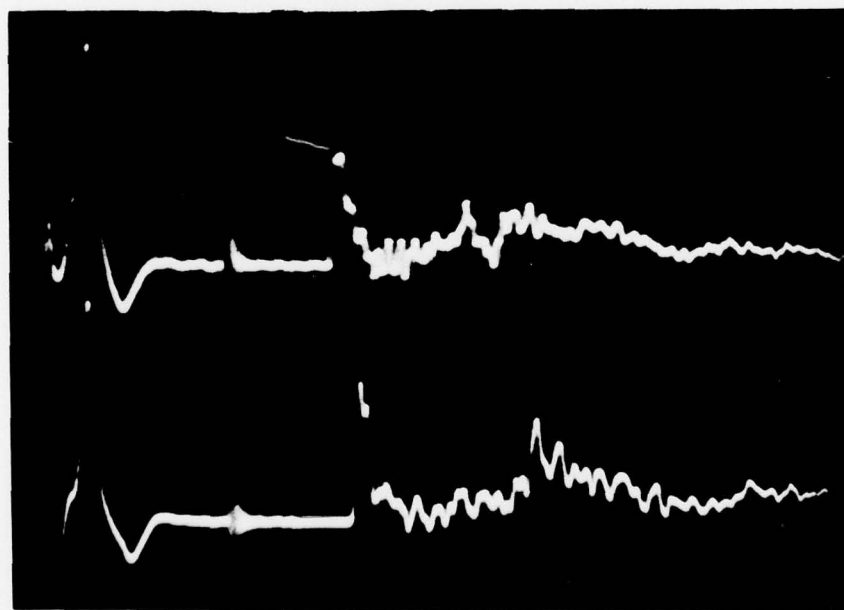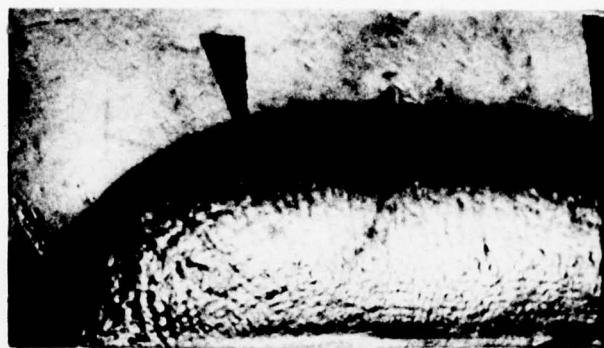
FIG·37 PHOTOCHEMICAL INITIATION OF DETONATION IN EQUIMOLAR H_2-Cl_2 MIXTURE AT 100 TORR
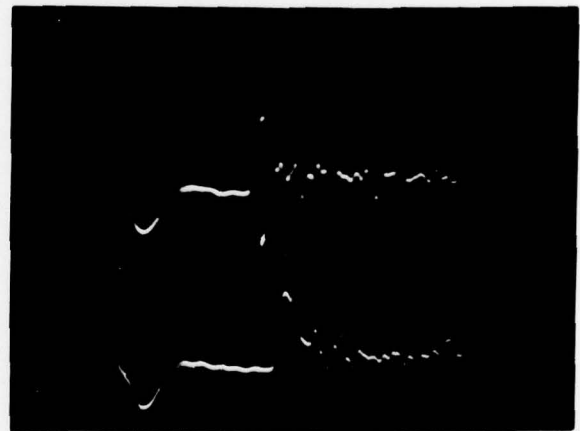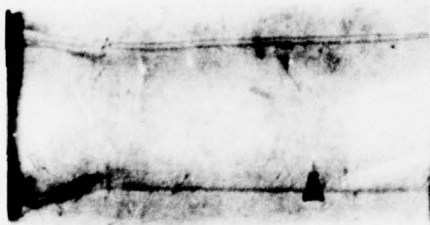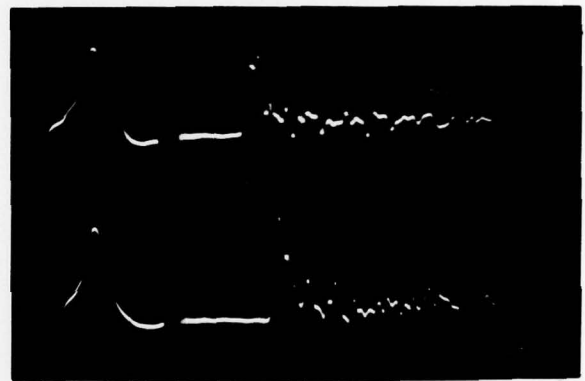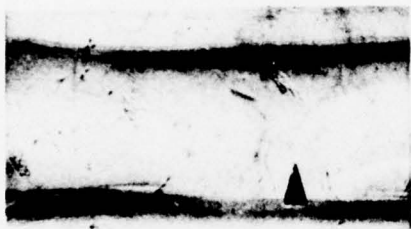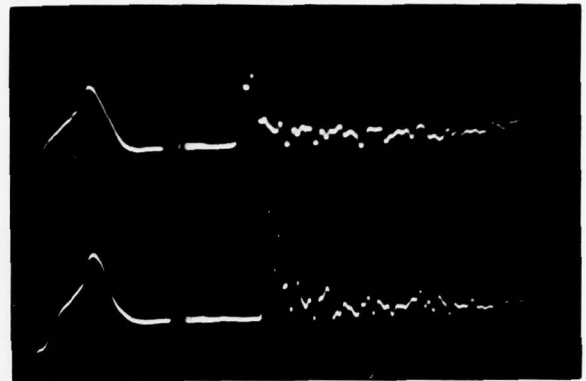
FIG. 38 EFFECT OF FLASH INTENSITY ON DETONATION PROPAGATION
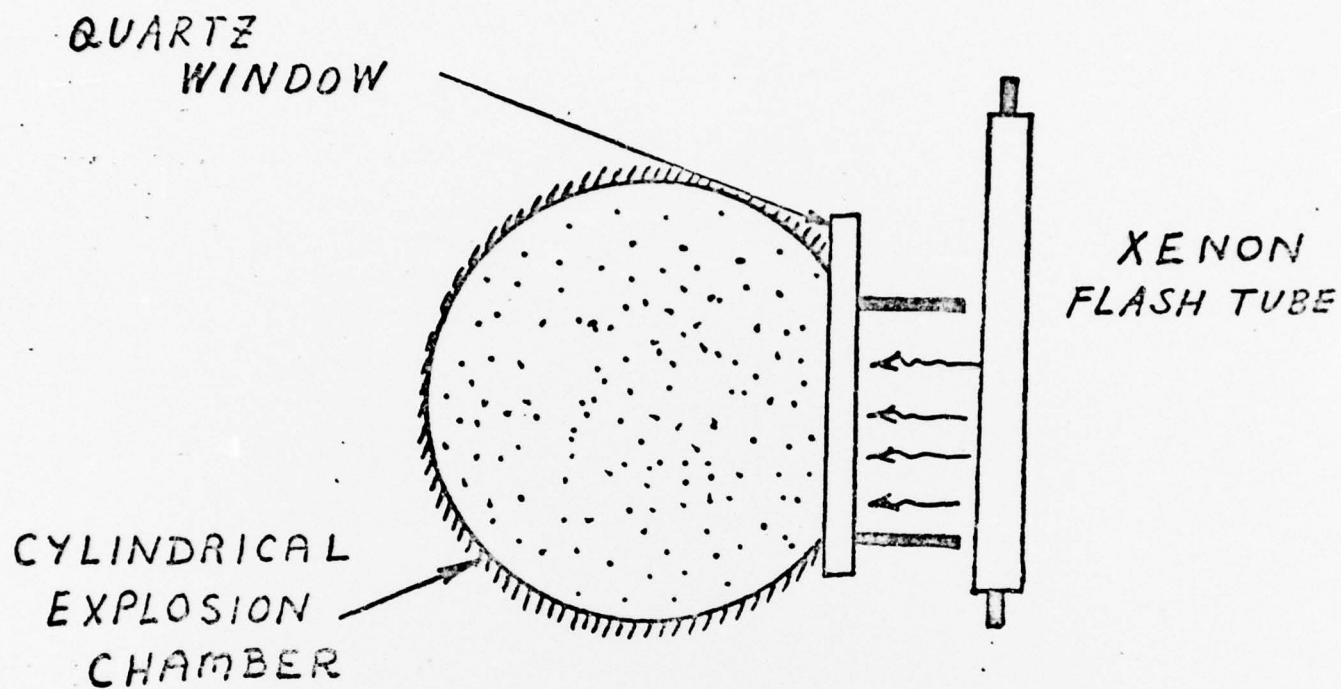
FIG. 39 PHOTOCHEMICAL INITIATION OF DETONATION IN THE CYLINDRICAL EXPLOSION CHAMBER

2CM

FIG.40 DEFLAGRATIVE, TRANSITIONAL AND DETONATIVE REGIMES OF PROPAGATION VIA PHOTOCHEMICAL INITIATION
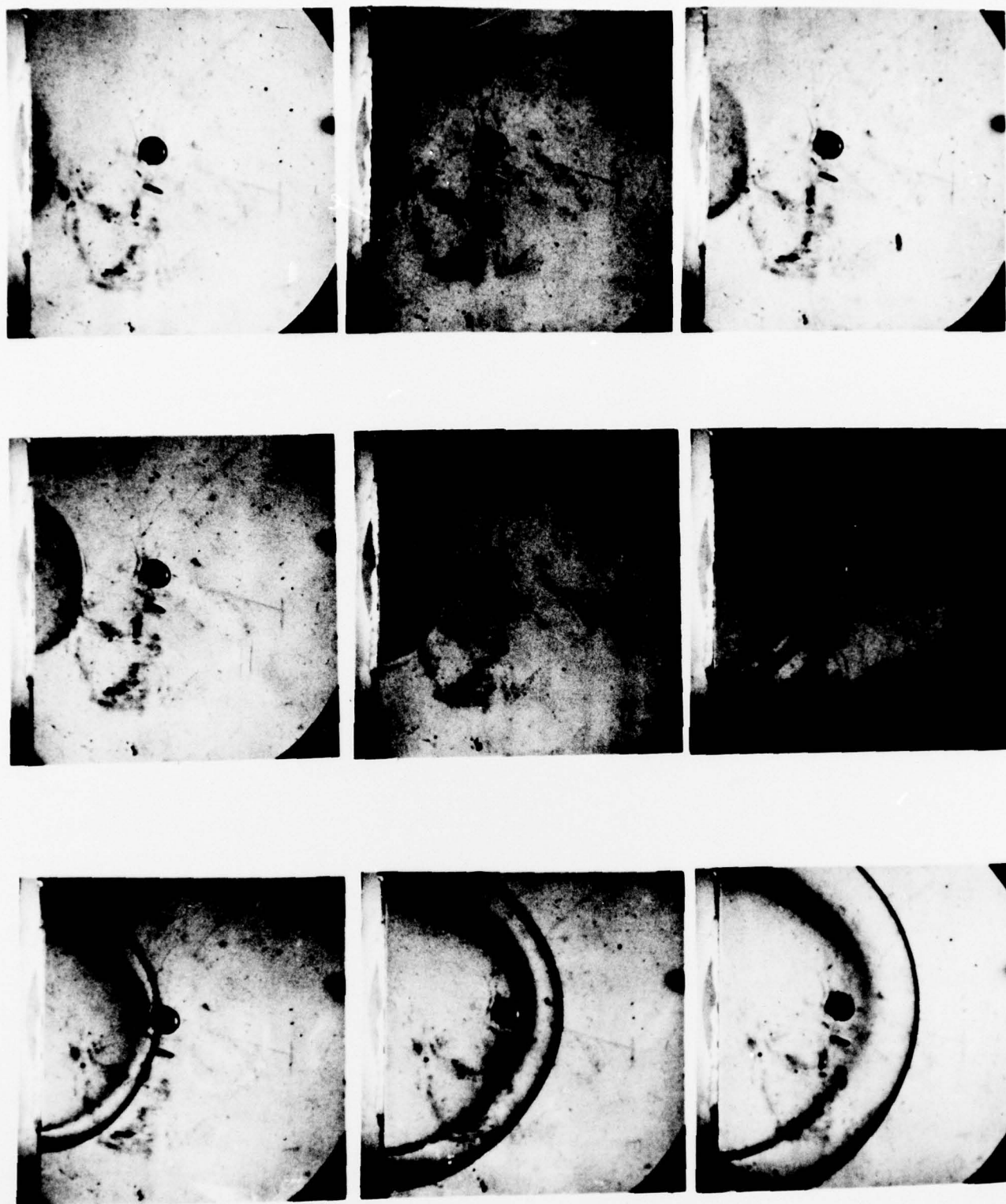
FIG. 41 PHOTOCHEMICAL INITIATION OF DEFLAGRATION IN EQUIMOLAR H_2-Cl_2 MIXTURE AT 100 TORR
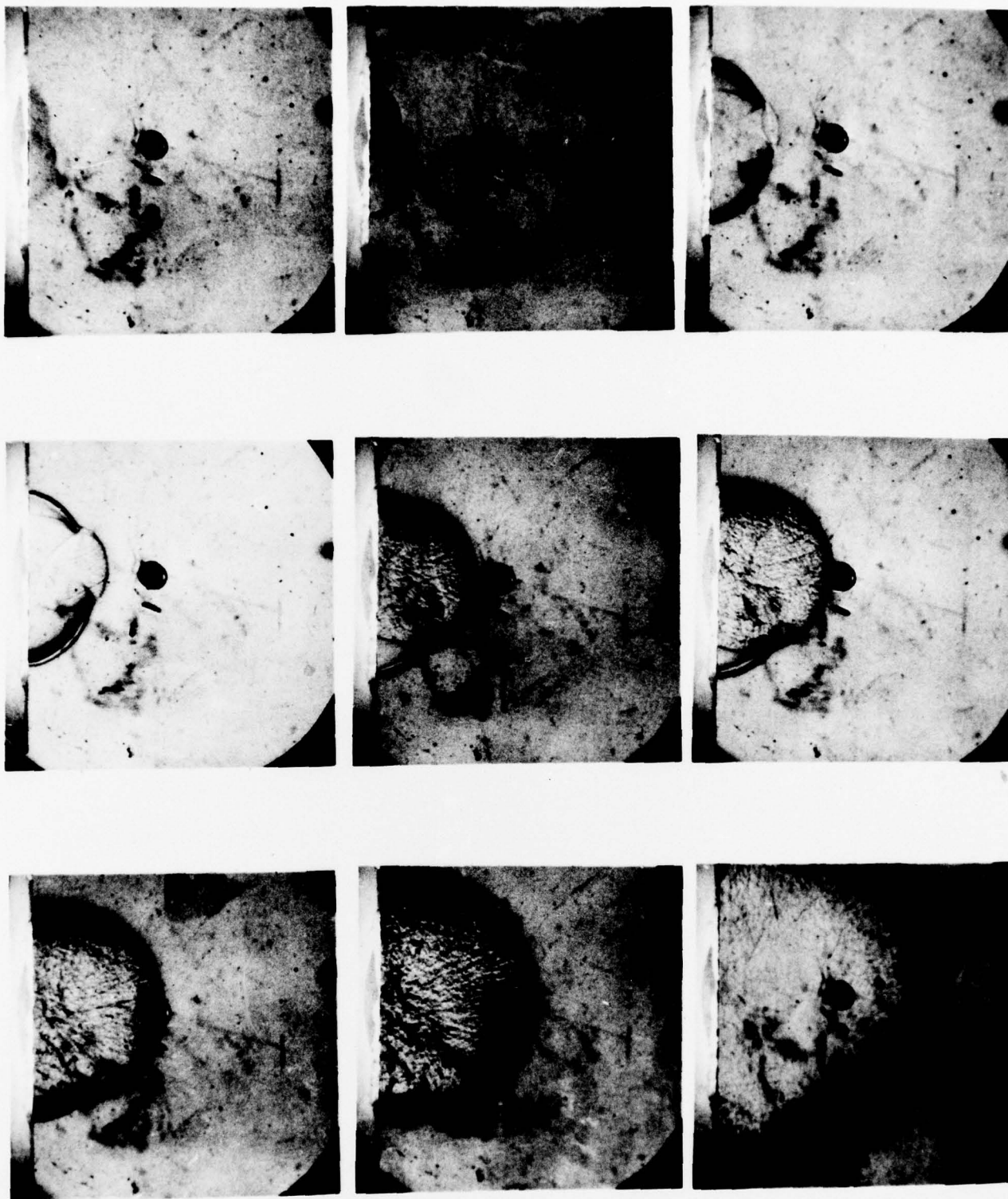
FIG. 42   TRANSITION   TO   DETONATION   OF   A
PHOTOCHEMICALLY   INITIATED   DEFLAGRATION

FIG·43 PHOTOCHEMICAL INITIATION OF DETONATION
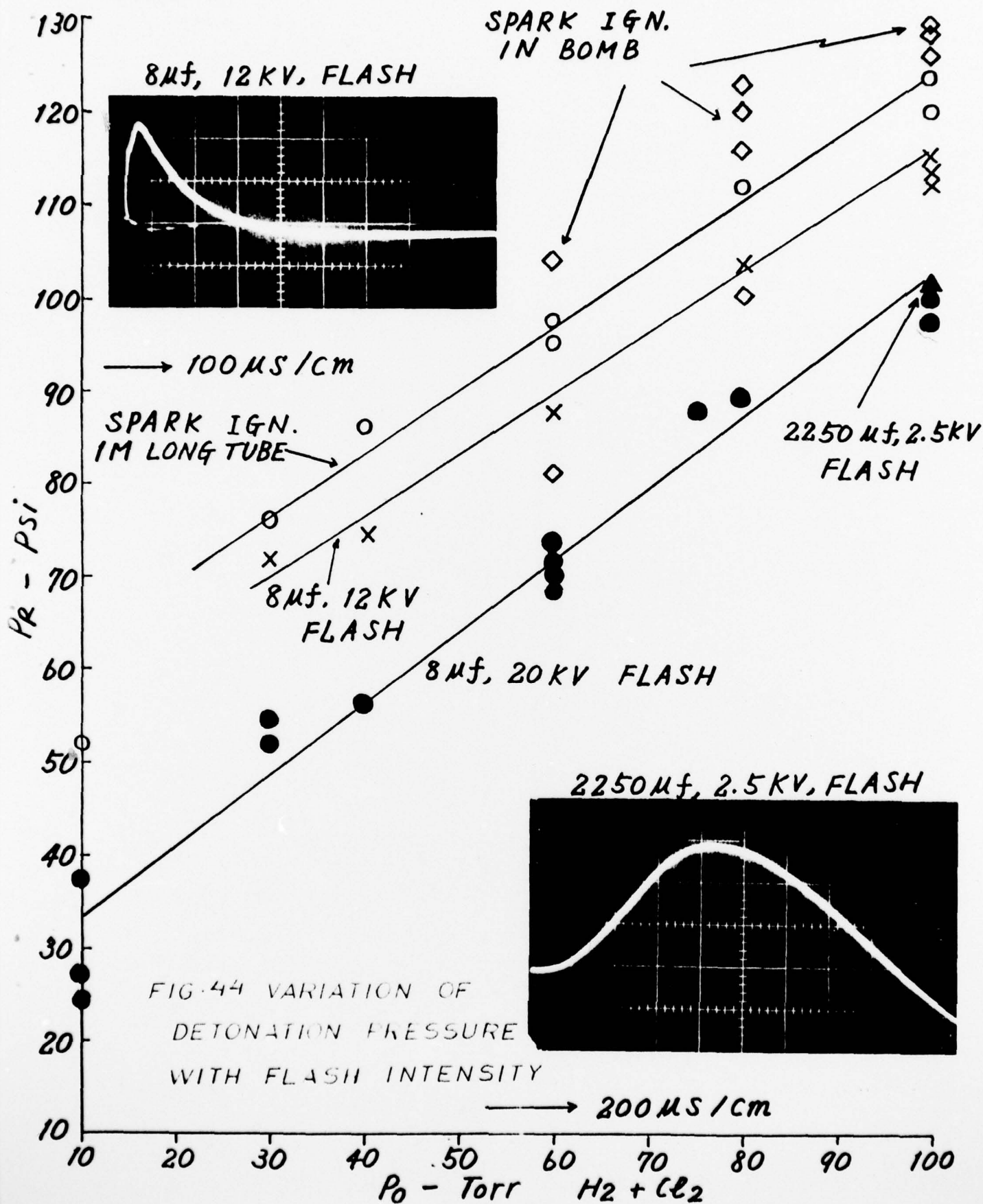IN EQUIMOLAR H_2-Cl_2 MIXTURE AT 100 TORR

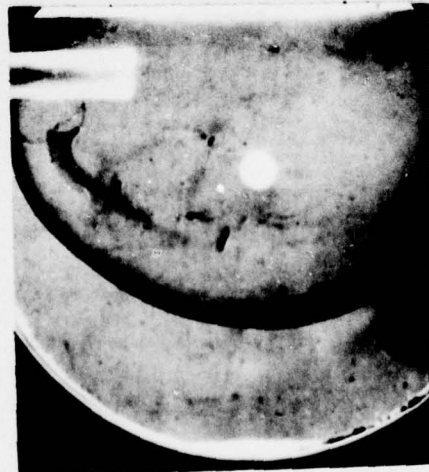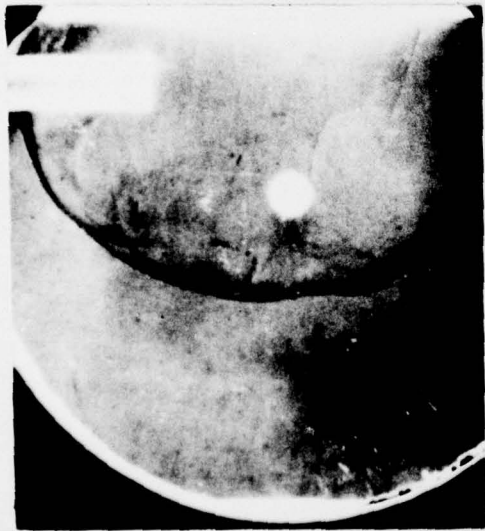FIG·44 VARIATION OF DETONATION PRESSURE WITH FLASH INTENSITY

FIG. 45 PHOTOCHEMICAL INITIATION OF A FLAME IN $C_2H_2-O_2$ SEEDED WITH NO_2

$2\,CM$

$t = 1000\,\mu s$

$t = 900\,\mu s$

$200\,\mu s/cm$

$200\,\mu s/cm$

FIG. 46 PHOTOCHEMICAL INITIATION OF A FLAME IN $C_2H_2 - O_2$ SEEDED WITH NO_2